SWELLING BEHAVIOUR OF NITRILE RUBBER IN ORGANIC LIQUIDS

by

SAMIR NAGUIB LAWANDY, M.Sc.

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Supervisor: C. M. Blow, Ph.D.

Institute of Polymer Technology

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SUMMARY

This research is concerned with the interaction of elastomers
and liquids, more specifically with volume changes of rubber in
liquids, particularly with nitrile rubbers and mineral oils ;
with free swelling and the effect of compressive strain on swelling
and set.

One particular aspect is to arrive at a method of quantitative
characterisation of commercial rubber mixes and organic liquids to
enable the volume change of a particular rubber in a particular
liquid to be calculated or estimated from data easily obtained about
the rubber and the liquid.

Basically, the polymer-liquid interaction constants and solubility
parameters for polymers of different acrylonitrile contents and
different grades of mineral oil and liquids of low boiling point have
been determined, from which the volume change of a particular mix and
a particular liquid can be estimated.

The extraction of soluble ingredients from rubber mixes by
liquids must be considered. In the case of low boiling liquids preextraction
of the rubber mix by the test liquid should be carried out before
swelling measurements. This extractable matter depends on the liquid
and the degree of swelling produced.

A method is given to study the effect of particle size and
structure of carbon black, the polymer content, the cure system and
cure time on the interaction between liquids and vulcanised rubber
mixes. These studies have shown that the interaction constant is
affected only by carbon black type. Further studies on the inter-
action constant (μ) have shown that liquids for which μ is less than
0.3 and greater than 0.7 should not be used for calculating the
crosslink density of vulcanised rubber.

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A satisfactory method has been given for restricted swelling of rubbers containing particulate fillers in liquids. The method has been extended to cover different types and amounts of filler and liquids. This method has also been developed for the identification of the type and amount of filler in a particular mix.

In the thesis an attempt is made to fit Einstein, Smallwood and Guth-Gold equations to the modulus results obtained from nitrile mixes with varying carbon black concentrations and type. No success was achieved but useful empirical formulae are given relating the network chain densities of pure gum mixes and filled rubber mixes to carbon black concentration.

The kinetic theory of elasticity has been shown to apply to vulcanisates based on the butadiene-acrylonitrile copolymers.

The thesis shows that the SCI system given by the Association of Hydraulic Equipment Manufacture (AHEM) can be replaced by another system dealing with the solubility parameter of oils.

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NOMENCLATURE and SYMBOLS

A_o Cross sectional area

a_1 Activity of solvent

C_1, C_2 Stress-Strain constants

C Volume concentration of filler

CS   Compression set

CS_e Swelling-corrected set

C_v Coefficient of variation

D Diffusion coefficient

d Thickness

E Modulus

E_x % volume extracted by low boiling liquid

E_x' % volume extracted by oil

$\bar{E}_x$ Mean extraction by volume

f_o Activity coefficient

f Force

f_s Shape factor (filler)

G, G' Molecular weight between two cross-links

ΔG Free energy

ΔH_m Heat of mixing

h_o Original thickness of sample

h_r Final thickness of sample

h_s Spacer thickness

h_e Corrected initial thickness

k Boltzman constant

M_t Amount of diffusant at time t

M_e Amount of diffusant at equilibrium

n_1 Number of moles of solvent

n_2 Number of moles of solute

N_1	Number of solvent molecules
N_2	Number of polymer molecules
N	Number of network chains
P	Penetration rate
P_o	Vapour pressure of solvent
P_1	Vapour pressure of solution
q	Constant for nitrile polymer - carbon black
R	Gas constant
S	Cross section diameter
ΔS_m	Entropy change
t	Time
T	Absolute temperature
ΔT	Temperature difference
V	Molar volume
V_m	Volume of mix containing 100 volume of polymer
ΔV_s	Strained swollen volume
ΔV_o	Unstrained swollen volume
ΔV_1	Equilibrium volume swelling by low boiling liquids (preextracted)
ΔV_2	Equilibrium volume swelling by oils (unextracted)
ΔV_3	Equilibrium volume swelling by oils per 100 volume of polymer in a 100 volume of mix
ΔV_x	Equilibrium volume swelling by oils (preextracted)
ΔV_s	Equilibrium volume swelling under compressive strain
$\overline{\Delta V}_1$	Mean swelling values
v_r	Volume fraction of rubber mix in the swollen gel
v_{ro}	Volume fraction of pure gum in the swollen gel
v_1	Volume fraction of solvent
v_2	Volume fraction of solute

$\Delta\omega$ Change in probability

W Stored energy

W_1 Weight in air before extraction

W_2 Weight in liquid before extraction

W_3 Weight in air after extraction

W_4 Weight in liquid after extraction

W_5 Weight in air after equilibrium swelling

W_6 Weight in liquid after equilibrium swelling

W_7' Weight in air after equilibrium swelling by oils (extracted samples)

W_8 Weight in water after equilibrium swelling by oils (extracted samples)

x_1 Mole fraction of solvent

x Submolecules

z Lattice constant

α_1 Constant for the solvent-solute system

δ_1 Solubility parameter of liquid

δ_2 Solubility parameter of solute

λ Extension ratio

σ Standard deviation

ρ Density

μ Interaction constant – polymer/liquid.

μ_s Reciprocal of lattice constant

ϕ Constant parameter for filler

ACN   Acrylonitrile content

l.b.l.   Low boiling liquid

S.P.   Solubility parameter

M.V.   Molecular volume

Reference Note

The Harvard system has been adopted: the author(s) and the year of publication are guided in the text. At the end of the thesis the references are listed in alphabetical order of first author with the section in which it refers.

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INTRODUCTION AND REVIEW OF RELEVANT PUBLISHED WORK

1.1 Objective of Investigation

Elastomeric seals have the advantages of good elasticity, low modulus, resistance to many chemicals and relatively high temperatures and are available in a wide range of hardness and sizes.

These seals are often in contact with one of the many types of organic liquids used in industry today; it is desirable to investigate the swelling of elastomers to understand more completely the phenomena involved.

The swelling of rubber involves a diffusion process by which the liquid is transported from one part of the sample to another. At the start of this process, the surface has a high liquid concentration, the liquid molecules subsequently diffusing into the bulk of the rubber. As this diffusion process proceeds, the dimensions of the rubber increase until the concentration of the liquid is uniform and equilibrium is achieved.

The amount of liquid that is taken up depends on; (i) the cohesive energy densities (square of solubility parameter) of the rubber and liquid (ii) the number and type of crosslinks in the vulcanisate which determine the modulus of the network and (iii) the amount and type of non-rubber ingredients in the vulcanisate.

Because, for many applications of seals, it is important to know how much liquid the elastomer absorbs and how fast, volumetric changes and penetration rates in free swelling are determined. The extraction of ingredients from the rubber

mix by solvents and liquids is also of importance. The swelling

process is reversible and, in the case of volatile liquids, on

drying out, the rubber returns to its original shape; usually,

however, the liquid extracts plasticizer and other soluble

constituents, so that the rubber shows a decrease in volume after

drying. The volume change on extraction is one of our interests

in this study.

In engineering applications as a seal, the elastomer is

under strain and therefore swelling tests under strain are also

carried out, recording the extent of recovery after release of

the strain. The development of set, representing incomplete

recovery from deformation, is time dependent and of considerable

importance.

The two cases for study are, therefore, free swelling and

swelling under strain. Nitrile rubber (butadiene-acrylonitrile

copolymer) possessing good oil and heat resistance was selected

for study because of its wide commercial usage in engineering

applications.

The study involved rubber compounding variations as follows:

(i)   the particle size and structure of the carbon black filler,

(ii)   the polymer content,

(iii)   the curing system,

(iv)   the curing time,

(v)   the acrylonitrile content of the polymer .

The liquids selected were mineral oils of the types used in hydraulic and other engineering applications; in addition solvents, in particular, acetone, toluene and chloroform, were used as swelling and extraction agents.

This work aimed to arrive at a method of quantitative characterisation of rubber mixes and organic liquids and oils so that the volume change of a particular mix in a particular liquid or oil can be estimated.

1.2   The Diffusion Process

The process of free swelling at a given temperature is a function of the variables:- time, test piece thickness and the viscosity of the liquid.

Crank (1956) predicts that the weight uptake at a given time is proportional to the square root of time. He reports that, for a plane sheet of thickness d, the ratio of the amount of diffusant M_t taken up at time t, to that absorbed at equilibrium, M_e, is given by the equation:

$$\frac{M_t}{M_e} = \frac{4D^{\frac{1}{2}}}{\pi^{\frac{1}{2}}} \; (t/d^2)^{\frac{1}{2}} \tag{1}$$

The value of D, termed the diffusion coefficient, can be deduced from of the plot of M_t versus $t^{\frac{1}{2}}$ which is a straight line, within the experimental error, up to a value for M_t/M_e of approximately 0.5.

The prediction was confirmed by Southern and Thomas (1967) who calculated the diffusion coefficient of liquids in cross-linked natural rubber. They used an equation derived from equation (1), for diffusion from two faces of a sheet of area large compared with its thickness, assuming that all absorbed liquid is contained in layer of swollen rubber of uniform concentration and the swelling proceeds by increasing the depth, d of the swollen layer. From this assumption the penetration rate:

$$P = \frac{d}{2M_e} \; \left(\frac{M_t}{t^{\frac{1}{2}}} \right) \tag{2}$$

If M_t is plotted against the square root of time, $M_t/t^{\frac{1}{2}}$ can be calculated and a value of P arrived at.

Comparing equations (1) and (2), the relation between the penetration rate and diffusion coefficient is given by:

$$D = \frac{\pi P^2}{4} \qquad (3)$$

Further studies were made by Blow et al (1968), concerned with the factors which affect the penetration rate, i.e. (i) the test piece shape and size, and (ii) the temperature. The rubber/liquid ratio has no effect but it is recommended that it be kept constant.

Blow gives an equation for O-rings of cross sectional diameter, S:

$$P = \frac{SM_t}{4M_e t^{\frac{1}{2}}} \qquad (4)$$

1.3 Thermodynamics of Polymer Solutions

Raoult's law states that the ratio of the vapour pressure of an ideal solution P_1 to that of the pure solvent P_o is equal to the mole fraction of solvent in the solution x_1.

$$P_1/P_o = x_1 \qquad (5)$$

Few solutions are ideal and equation (5) is seldom obeyed.

Solutions of polymers, having a high molecular weight, show a wide deviation except when they are very dilute. A modified equation is:

$$P_1/P_o = x_1 \ f_o = a_1 \qquad (6)$$

where f_o is the activity coefficient and a_1 is the activity of the solvent. The number of ways in which the solvent molecules can be arranged on the lattice can be related to the change in probability Δw and the corresponding entropy change ΔS_m by

$$\Delta S_m = k \ \ln \ \Delta w \tag{7}$$

where k is Boltzman Constant. If the solute and solvent molecules can replace each other (random mixing) then;

$$\Delta S_m = - R (n_1 \ln x_1 + n_2 \ln x_2) \tag{8}$$

where n_1 and n_2 are the number of moles of solvent and solute respectively. If each polymer molecule in a polymer solution is composed of x chain segments, Flory (1941) and Huggins (1942) assumed that each point of a lattice of coordinate number z could be occupied either by a solvent molecule or by a polymer segment. They counted the number of ways of placing N_1 solvent molecules and N_2 polymer molecules each composed of x submolecules on N_1 x N_2 molecules, this leads to the expression:

$$\Delta S_m = - R \left[n_1 \ln \frac{N_1}{N_1 + x N_2} + n_2 \ln \frac{x N_2}{N_1 + x N_2} \right] \tag{9}$$

Replacing $\dfrac{N_1}{N_1 + x N_2}$ and $\dfrac{x N_2}{N_1 + x N_2}$ by v_1 and v_2 respectively

$$\Delta S_m = - R \left[n_1 \ \ln v_1 + n_2 \ln v_2 \right] \tag{10}$$

from which

$$\overline{\Delta S}_m = - R \left[\ln (1 - v_2) + v_2 (1 - {}^1/_x) \right] \tag{11}$$

1.4 The Heat of Dilution

A molecule in a solvent is surrounded by a number of similar molecules which exert an attractive force *on* each *to* other. The force of attraction depends on the nature of these molecules. In mixing two liquids of different intermolecular forces, the generated force of attraction will not be equal to the sum of individual forces. Hildebrand (1950) has suggested that the heat absorbed by mixing ΔH_m is given by:

$$\Delta H_m = v_1 \ v_2 \ V \ (\delta_1 - \delta_2)^2 \qquad (12)$$

where δ_1 and δ_2 are the solubility parameter of solvent and solute and V is the molar volume of the mixture. The heat of dilution is given by:

$$\Delta \bar{H} = V \ (\delta_1 - \delta_2)^2 \ v_2^2 = \alpha_1 \ v_2^2 \qquad (13)$$

where

$$\alpha_1 = V \ (\delta_1 - \delta_2)^2 \qquad (14)$$

and α_1 is a constant for the system, V is the molar volume of solvent. This equation can be used for polymer solvent ~~relation.~~ *systems.*

1.5 The Free Energy of Dilution

The mixing of liquids is generally accompanied by an increase in entropy and absorption of heat (or energy). The free energy can join these two factors and liquids will mix as long as the process involves a decrease in free energy. The increase in free energy ΔG is related to the heat energy ΔH and the entropy ΔS by the relation

$$\overline{\Delta G} = \overline{\Delta H} - T \ \overline{\Delta S} \qquad (15)$$

Substituting equation (11) and (13) in (14)

$$\Delta \bar{G} = \alpha_1 v_2^2 + RT \left[\ln (1-v_2) + v_2 (1-\tfrac{1}{x}) \right]$$

This can be simply written

$$\Delta \bar{G} = RT \left[\ln (1-v_2) + (1-\tfrac{1}{x}) v_2 + \frac{\alpha_1}{RT} v_2^2 \right] \qquad (16)$$

Huggins gives a similar expression for the change in free energy including a lattice coordinate number z

$$\Delta G_1 = RT \left[\ln (1-v_2) + \frac{(1-\tfrac{1}{x})}{2} z \ln(1-2v_2/z) + \frac{\alpha_1}{RT} v_2^2 \right] (17)$$

Expanding the second logarithmic term and ignoring the terms beyond the second term and considering x is large, then

$$\Delta G_1 = RT \left[\ln (1-v_2) + v_2 + \mu v_2^2 \right] \qquad (18)$$

where $\mu = \tfrac{1}{z} + \alpha_1/RT$ $\qquad\qquad (19)$

The quantity μ is called the polymer-solvent interaction constant. This value is very important in the relation between swelling and stress-strain properties of a polymer.

From equation (14) and (19)

$$\mu = \tfrac{1}{z} + V (\delta_1 - \delta_2)^2 / RT \qquad\qquad (20)$$

where z depends on the type of lattice. This equation is of special importance for calculating the solubility parameter of a polymer or a solvent.

1.6 Swelling of Rubber Network

The swelling of rubber is opposed by elastic retraction of the network. At equilibrium state the two effects are balanced and the free energy ΔG will be considered to be the sum of free energy of mixing ΔG_m and the free energy arising from the expansion of the network structure ΔG_{el}. The rubber-like elasticity theory can be used to correlate these two factors.

This theory depends on the fact that rubber contains flexible long chain molecules. Unvulcanised rubber consists of a very large number of these chains the segments of which have the ability to rotate about chemical bonds and crosslinks are introduced between these molecules by which a 3-dimensional network is built.

To derive strain relations the entropy of rubber in both strained and unstrained state must be calculated by summing the entropies of all individual chains in the network.

Consider a unit cube of rubber which deformed to a rectangular parallelopiped by strain with extension ratios λ_1, λ_2 and λ_3. The change in entropy ΔS will be

$$\Delta S = -\tfrac{1}{2} N k (\lambda_1^2 + \lambda_2^2 + \lambda_3^2)^{-3} \qquad (21)$$

where N is the number of network chains and k is Boltzman's Constant.

Assuming that the internal energy is constant. The stored energy W is given by

$$W = \tfrac{1}{2} N k T \left[\lambda_1^2 + \lambda_2^2 + \lambda_3^2 - 3 \right] \qquad (22)$$

Flory (1950) has derived an alternative relation for change in entropy on deformation

$$\Delta S = -\tfrac{1}{2} N k \left[\lambda_1^2 + \lambda_2^2 + \lambda_3^2 - \ln (\lambda_1 \lambda_2 \lambda_3) \right] \quad (23)$$

The term $\lambda_1 \lambda_2 \lambda_3$ arises from the permutation crosslinked network chains among each other throughout the volume of rubber. This term does not affect the stress-strain relation because on deformation the volume of rubber is substantially unaltered, but does affect the equilibrium swelling. Flory has also reported that the extraction can be introduced in calculation of equilibrium swelling or can be neglected if it is comparatively small.

If a crosslinked network is swollen so that the volume fraction of rubber is v_r, then the extension ratios λ_1', λ_2' and λ_3' referred to the swollen unstrained state are given by $\lambda_1' = \lambda v_r^{1/3}$ where λ_1 referred to dry swollen unstrained state.

The change in entropy from dry unstrained state to swollen strained state per unit volume in unswollen state

$$\Delta S' = -\tfrac{1}{2} N k \; v_r^{-2/3} (\lambda_1'^2 + \lambda_2'^2 + \lambda_3'^2 - 3) \quad (24)$$

The stored energy per unit swollen volume

$$W = -T \Delta S = \tfrac{1}{2} N k T \; v_r^{1/3} (\lambda_1'^2 + \lambda_2'^2 + \lambda_3'^2 - 3) \quad (25)$$

which is identical with equation (22) except the additional term $v_r^{1/3}$.

For most types of homogenous strain the three principle extension ratios, λ_1, λ_2 and λ_3 which are under normal conditions

$$\lambda_1 \cdot \lambda_2 \cdot \lambda_3 = 1 \quad (26)$$

by differentiation

$$\frac{d\lambda_1}{\lambda_1} + \frac{d\lambda_2}{\lambda_2} + \frac{d\lambda_3}{\lambda_3} = 0 \qquad (27)$$

$$\therefore \quad \frac{d\lambda_3}{\lambda_3} = - \left(\frac{d\lambda_1}{\lambda_1} + \frac{d\lambda_2}{\lambda_2} \right) \qquad (28)$$

If f_1, f_2, f_3 are forces applied on a cube of rubber of unit area to produce an extension λ_1, λ_2 and λ_3 then the change in work done

$$dW = f_1 \, d\lambda_1 + f_2 \, d\lambda_2 + f_3 \, d\lambda_3 \qquad (29)$$

using equation (28) in (29)

$$dW = f_1 \, d\lambda_1 + f_2 \, d\lambda_2 - f_3\lambda_3 \frac{d\lambda_1}{\lambda_1} - f_3\lambda_3 \frac{d\lambda_2}{\lambda_2}$$

which can be written simply as

$$dW = (\lambda_1 f_1 - \lambda_3 f_3) \frac{d\lambda_1}{\lambda_1} + (f_2\lambda_2 - f_3\lambda_3) \frac{d\lambda_2}{\lambda_2} \qquad (30)$$

The change in stored energy can be calculated from equation (25).

$$dW = NkT \; v_r^{1/3} \left(\lambda_1 \, d\lambda_1 + \lambda_2 \, d\lambda_2 + \lambda_3 \, d\lambda_3 \right) \qquad (31) \qquad \times$$

Eliminating $d\lambda_3$ by using equation (28)

$$dW = NkT \; v_r^{1/3} \left[(\lambda_1^2 - \lambda_3^2) \frac{d\lambda_1}{\lambda_1} + (\lambda_2^2 - \lambda_3)^2 \frac{d\lambda_2}{\lambda_2} \right] \qquad (32)$$

from equation (30) and (32)

$$\lambda_1 f_1 - \lambda_3 f_3 = NkT \; v_r^{1/3} (\lambda_1^2 - \lambda_3^2) \qquad (33)$$

In simple extension $f_2 = f_3 = 0$ and $\lambda_2 = \lambda_3 = \lambda_1^{-\frac{1}{2}}$

and thus from equation (33)

$$f_1 = NkT \ v_r^{-1/3} \ (\lambda_1 - \lambda_1^{-2}) \tag{34}$$

and for dry rubber

$$f_1 = NkT \ (\lambda_1 - \lambda_1^{-2}) \tag{35}$$

1.7 The Relation of Crosslink Density to Stress Strain Behaviour

The kinetic theory of elasticity relates the force, f, to extend a sample of cross-sectional area A_o to an extension ratio λ, to the degree of crosslinking $v = \frac{1}{2G}$ the number of gram moles of crosslink per unit gram of rubber

$$f = \frac{\rho RT \ Ao}{G} \ (\lambda - \lambda^{-2}) \tag{36}$$

where ρ is the density of polymer and R = gas constant. Mooney-Rivlin (1951) have shown that for simple extension the stress strain curve often follows is the relation

$$f/A_o(\ \lambda - \lambda^{-2}) = 2C_1 + 2C_2\lambda^{-1} \tag{37}$$

and a plot of experimental data in the form $f/A_o(\lambda - \lambda^{-2})$ vs λ^{-1} should yield to a straight line of slope $2C_2$ and intercept $2C_1$.

Comparing this formula to the kinetic theory the intercept $2C_1 = \frac{\rho RT}{G}$ and $2C_2$ should be equal to zero. The stress-strain behaviour for swollen rubber will be given by the equation

$$f/A_o(\lambda - \lambda^{-2}) = 2 \ v_r^{1/3} \ (C_1 + C_2\lambda^{-1}) \tag{38}$$

1.8 Stress-strain behaviour and the Degree of Swelling

Equation (25) can be used to explain this relation. The Gibbs free energy of dilution $\Delta G/\Delta n$ of a polymer solution by a solvent is derived as

$$\Delta G/\Delta n = RT \left[\ln (1-v_r) + v_r + \mu v_r^2 \right] \tag{39}$$

where Δn is the number of moles of liquid in the swollen rubber. At equilibrium the free energy is balanced by that from the extension network during swelling. The following subjects will be studied:

(i) Free Swelling

We shall consider a cubic unit of cross-linked network in contact with a solvent, it will be under stresses f_1, f_2, f_3 applied to its surface, and it will deform to dimension λ_1, λ_2, λ_3 of a parallelopiped. Then if a liquid and polymer mix without change in volume, then

$$\lambda_1 \ \lambda_2 \ \lambda_3 = v_r^{-1} = 1 + nV \tag{40}$$

where n is the number of moles of liquid of molar volume V in the polymer. If further Δn is absorbed while λ_2 and λ_3 are held constant then the total work done by external forces can be obtained by differentiating equation (40) with respect to λ_1

$$W = f_1 \ \lambda_2 \ \lambda_3 \ \Delta \lambda_1 = f_1 \ V\Delta n \tag{41}$$

As the change in internal energy is zero, then the change in free energy of the network due to deformation is given by $T\Delta S$ using equation (21) and (41)

$$\Delta G = NkT \ \lambda_1 \ \Delta\lambda_1 = NkT\lambda_1 \ V\Delta n/\lambda_2 \ \lambda_3 \tag{42}$$

If the volume change of the whole system of rubber and liquid is assumed to be zero

$$W = f_1 V \Delta n = NkT\lambda_1 V \Delta n / \lambda_2 \lambda_3 + RT \left[\ln(1-v_r) + v_r + \mu v_r^2 \right] \Delta n \quad (43)$$

Putting $Nk = \rho R/G$ where ρ is the density of rubber and G the number of average molecular weight of the network chain, then,

$$t_1 = RT \, V^{-1} \left[\ln(1-v_r) + v_r + v_r^2 + \rho V G^{-1} v_r \lambda_1^2 \right] \quad (44)$$

The same relation is hold for t_2 and t_3. For free swelling $f_1 = f_2 = f_3 = 0$ and that means $\lambda_1 = \lambda_2 = \lambda_3$

i.e.

$$\lambda_1^3 = v_r^{-1} \quad \text{and} \quad \lambda_1^2 = v_r^{-2/3}$$

and equation (44) becomes

$$\ln(1-v_r) + v_r + \mu v_r^2 = - \frac{\rho V}{G} \, v_r^{1/3} \quad (45)$$

and if Flory modification equation (23) is used i.e. an additional term due to permutation crosslinked network, which is

$$- \frac{\rho V}{2G} \ln(\lambda_1 \lambda_2 \lambda_3) = - \frac{\rho V}{2G} \ln \lambda^3 = - \frac{\rho V}{2G} \ln v_r^{-1} = - \frac{\rho V}{2G} v_r$$

Equation (45) becomes:

$$\ln(1-v_r) + v_r + \mu v_r^2 = - \frac{\rho V}{G} \left(v_r^{1/3} - \tfrac{1}{2} v_r \right) \quad (46)$$

This equation is known by Flory-Rehner relation..

(ii) Swelling Under Simple Strain.

At simple strain $f_2 = f_3 = 0$ and $\lambda_2^2 = \lambda_3^2 = (\lambda_1 v_r)^{-1}$ and equation (44) at equilibrium becomes

$$\ln(1-v_r) + v_r + \mu v_r^2 = - \frac{\rho V}{G \lambda_1} \quad (47)$$

This equation was given by Flory and Rehner (1944) in which they related the volume fraction of rubber v_r in the swollen gel to a stretch factor λ_1.

Taking v_r to be small (at large swelling) expansion of the logarithm term led to the following equation

$$\frac{1}{\Delta V_s} = \left[\frac{\rho V}{G} \times \frac{1}{\lambda_1(\frac{1}{2}-\mu)} \right]^{\frac{1}{2}}$$

where ΔV_s is the strained swollen volume. Hence writing V_0 for swelling volume in the unstretched swollen condition.

$$\frac{\Delta V_s}{\Delta V_0} = \left(\frac{\lambda_1}{\lambda_0} \right)^{\frac{1}{2}} \tag{48}$$

Treloar (1950) extended the theoretical treatment and showed the validity for homogenous strain and compression.

Blow, Exley and Southwart (1969) also made measurements of equilibrium swelling under unidirectional compression. They used different spacer thickness between metal plates, and showed that the strained swollen volume ΔV_s is proportional to (100-percentage compression)$^{\frac{1}{2}}$.

1.9 The Solubility Parameters of Rubber and Liquid

It has been shown (equation 20) that the polymer-liquid interaction constant μ depends on the difference in the squares of the solubility parameters of the liquid δ_1 and the polymer δ_2. Putting $\frac{1}{2} = \mu_s$ equation (20) becomes

$$\mu = \mu_s + V/RT \, (\delta_1 - \delta_2)^2 \tag{49}$$

Bristow and Watson (1954) give a more suitable form for the equation for calculating δ_2 (derived from equation 49)

$$(\delta_1^2/RT) - (\mu/V) = (2\delta_2/RT) \, \delta_1 - (\delta_2^2/RT) - (\mu_s/V) \tag{50}$$

A plot of the left side of equation (50) against δ_1 should give a straight line. From both the slope (and the intercept) of this line δ_2 can be calculated.

1.10 The Modulus of Filler Loaded Rubbers

The modulus of filled rubber vulcanisates depends, in general, on the particle size of the filler. This and other phenomena suggests a rubber/filler interaction.

Smallwood adopted the well-known Einstein equation, relating the viscosity increase to the volume particles suspended in a liquid:-

$$E = E_o \, (1 + 2.5 \, C) \tag{51}$$

where E and E_o are the moduli of filled and unfilled vulcanisates respectively, and C is the volume fraction of the filler in the mix. Equation (51) holds only for low concentrations of filler. Guth and Gold give a modified equation:-

$$E = E_o \, (1 + 2.5 \, C + 14.1 \, C^2) \tag{52}$$

where the last term is due to the interaction between two particles. These two equations (51, 52) have been shown to hold for large particles of carbon black where the rubber filler interaction is small. For non-spherical particles, Guth introduced a shape factor f_s and proposed:-

$$E = E_o \, (1 + .67 \, f_s \, C + 1.62 \, f_s^2 \, C^2) \tag{53}$$

Section 2

Experimental Procedures

2.1 **Introduction**

This section covers the materials used and the mixing

procedures. As the study involved rubber compounding variations,

the details of the compound formulations are deferred until Section 3.

A short summary is also included of the physical testing methods

and the determination of acrylonitrile content of the polymers and

the molecular weights of the oils. The procedures for measuring free

swelling and swelling under compressive strain are also described in

this section.

2.2 **Materials**

2.2.1 Polymers: Six nitrile polymers with acrylonitrile contents 20,
                    34.4
27.3, 28.7,/40.7 and 44.1; commercial names and numbers:- Tylac 109A,

Butakon A2503, Polysar Krynac 802, Butakon A3003 and A4003 and Tylac

113A respectively. These are summarised in Table (2.1).

Table 2.1 Trade name and nitrile contents of polymers

Trade name and grade	Supplier	% ACN
Krynac 802	Polysar Corporation	28.7
Butakon A2503	Revertex Ltd.	27.3
Butakon A3003	" "	34.4
Butakon A4003	" "	40.7
Tylac 109A	Standard Brands	20.0
Tylac 113A	" "	44.1

2.2.2 Carbon blacks: Four carbon blacks of different particle sizes

were employed as fillers:- Fine thermal (FT), Semi-reinforcing Furnace

(SRF), Fast extruding Furnace (FEF) and High Abrasion Furnace (HAF);

commercial numbers:- Sterling FT, Sterling S-1, Sterling 50 and

Vulcan 3 respectively. The essential characteristics of the four

blacks are summarised in the following Table (2.2).

Table 2.2 Properties of carbon blacks

Black type	Particle diameter in nm.	Structure cm^3 DBP/100g ASTM D2414	Relative reinforcing effect	Surface area m^2/g
FT	180-200	33	38	17
SRF	70-95	70	46	35
FEF	39-55	120	75	65
HAF	28-36	105	100	94

(Relative reinforcing is based on abrasion resistance of tyre tread mix at 50 phr). From Blow, Rubber Technology and Manufacture (1971), p.233, 185.

2.2.3 Vulcanising ingredients: since sulphur is less soluble and less dispersible in nitrile rubber than in other rubbers, a magnesium carbonate coated sulphur (MC) was used. Zinc oxide and stearic acid, as activators, and accelerators mercaptobenzthiazole (MBT), cyclohexyl-benzthiazol sulphenamide (CBS) and tetramethyl thiuram disulphide (TMTD) were used.

2.2.4 The antioxidant was octylated diphenylamine (Nonox OD). To minimise errors the curing ingredients and the antioxidant were master-batched in some mixes.

2.2.5 Oils: ASTM reference oils nos. 1 and 3, a 50/50 mixture of ASTM$_1$, and ASTM$_3$, DTD 585, Shell Tellus 27, Mobil Stock 23 and Mobil Stock 27; the latter two being, respectively solvent and acid refined naphthenic neutral oils of the same viscosity (20.5 cSt at 100°).

2.2.6 Low boiling organic liquids: The following were used for swelling and extraction: acetone, toluene, chloroform, n-hexane, n-heptane, cyclohexane, n-butanol and formic acid. The table 2.3 gives the characteristics of these solvents.

Table 2.3 Properties of Low boiling liquids

Solvent	Molecular Weight	Specific Gravity	Molecular Volume	Solubility Parameter
Acetone	58.08	0.790	74.00	9.712
Toluene	92.14	0.862	106.9	8.907
Chloroform	119.38	1.474	80.70	9.240
n-hexane	86.18	0.665	131.50	7.242
n-heptane	100.21	0.680	147.50	7.423
Cyclohexane	84.66	0.780	108.70	8.182
n-Butanol	74.12	0.808	91.73	11.250
Formic acid	46.03	1.203	38.26	13.50

From Bristow and Watson Trans. Farad. Soc. 54, No.11 Nov (1958)p.1731

2.3 Mixing Procedure and Test Piece Preparation

Mastication and mixing were   carried out on a two roll
mill (12" x 6") operating at a friction ratio of 1.25 : 1. Small
pieces of the polymer were repeatedly passed through at a narrow
nip setting until the material was plastic enough to receive the
accelerators, antioxidants and activators. When the mix was
completely uniform, the carbon black was added and finally the
sulphur. The mix was taken off, rolled and repeatedly passed
through the nip to ensure homogeneity. Vulcanised sheets (from
which test pieces were cut) and O-rings were obtained by
moulding in an electrically heated platen press at 150°C for
the times stated.

2.4 Rheometer Tests

The cure times for the different mixes were estimated from torque versus time plots obtained using the Monsanto oscillating disc rheometer. The torque required to oscillate a rotor embedded in the test piece which is confined in a cylindrical cavity at the desired curing temperature (150°C) is determined. The oscillation is $\pm 3^{\circ}$ and a biconical shaped disc is used to provide uniform shear strain and rate of shear within the sample. As vulcanization proceeds, the torque required to shear the rubber increases and a curve of torque versus time is generated. The torque value is directly related to the shear modulus of the rubber. The effect of compound changes on viscosity can be determined from the initial portion of the curve while, from the latter portion, the rate of vulcanisation and the modulus of the vulcanisate can be estimated. To calculate the 90% cure time the following formula is used.

$$90\% \text{ cure time} = (t_2 - t_1) \, 0.9 + t_1 \qquad (54)$$

where t_1 and t_2 are the times to minimum and maximum torque values. The term t_1 is included in this equation to correct for the heat transfer through the sample.

2.5 Physical Testing of Vulcanizates

2.5.1 Hardness: (B.S. 903 Part A20) Hardness determinations were carried out using the Wallace Dead-Load hardness tester in accordance with the above standard and the results expressed as International Rubber Hardness Degrees (IRHD). The test piece thickness was 10 mm.

2.5.2 Tensile stress-strain properties (B.S. 903 Part A2): Dumbbell test pieces were elongated to breakage using a Hounsfield pendulum type tensometer. From the plot of load

versus elongation, the stress at 100% strain, the stress and percentage elongation at break were obtained.

2.5.3 Stress-strain relationship at low strains.

In these determinations a test piece 100 mm x 5 mm x 1 mm has been used. The thickness and width were measured accurately. Samples were clamped vertically and stretched to different accurately known extensions, and allowed to relax for 90 sec; after which time the stress produced is balanced by weights using a triple beam balance. An accurate value of the initial length was obtained using a series of small loads at the beginning of the experiment.

For each known extension ratio λ, the value $(\lambda-\lambda^{-2})$ is calculated and plotted against the force applied; the slope of the line is determined and from this $G = \dfrac{(\lambda-\lambda^{-2})\rho RTA_o}{f}$ is obtained; ρ = the density of the rubber, R = gas constant and T is the absolute temperature.

2.6 The determination of acrylonitrile content: B.S. 903 Parts B11 and B12

The determinations of acrylonitrile content were carried out using $\times\times$ BUCHI nitrogen determination apparatus. The test piece was 0.1 gm of the polymer.

2.7 The determination of the Molecular Volume of Oils

The vapour pressure osmometer (KNAUER) has been used for determining the molecular weight of the seven oils used. Four solutions in toluene of concentrations 0.125, 0.250, 0.50 and 1% w/w are used. The instrument is set to zero by syringing a drop of solvent onto each of the two thermistors. If one solvent drop is replaced by a drop of solution, this latter will adjust to a higher temperature: the temperature difference ΔT between the two thermistors is proportional to the vapour pressure difference of the two drops.

The molecular weight of the oil can be obtained by extrapolating the relation between $\dfrac{\Delta T}{C}$ and C to C=0 and using the

formula

$$M.W. = \frac{K}{\frac{\Delta T}{C} \bigg/_{C}}$$

$$C \rightarrow 0$$

(55)

Where K is the calibrated constant for toluene; $C =$ concentration of oil in toluene. The specific gravity of the oils was determined by a hydrometer and hence the molecular volume calculated.

2.8 Extraction Techniques – low boiling liquids (see 2.2.6)

A rectangular test piece of size 15 x 15 mm cut from a moulded sheet of thickness 1 mm is weighed in air (W_1) and in the liquid (W_2). The sample is extracted at room temperature in a stoppered glass bottle containing about 40 cm^3 of the liquid for 72 hr. The sample is then removed and placed in an oven at $70^\circ C$ for 24 hr then weighed again in air (W_3) and in liquid (W_4).

The percentage volume extracted is calculated as:

$$E_x \text{ by volume} = \frac{(W_1-W_2) - (W_3 - W_4)}{(W_1 - W_2)} \quad x \quad 100$$

(56)

2.9 Free Swelling Measurements

2.9.1 Volatile liquids

The sample used for extraction is also weighed in air (W_5) and in the liquid (W_6) in the equilibrium swollen condition. In the case of highly volatile liquids, the test piece is weighed in liquid, withdrawn from the liquid, excess being removed by means of a filter paper; a stop watch is started and with the test piece hanging on the balance, the weight is recorded every 30 secs for 120–180 secs; the accurate weight is obtained by plotting

the weights against the square root of time and the resultant straight line extrapolated to zero time. Typical plots are given in Fig. 2.1. The equilibrium volume swelling ΔV_1 is calculated as

$$\Delta V_1 = \frac{(W_5 - W_6) - (W_3 - W_4)}{(W_3 - W_4)} \times 100 \qquad (57)$$

2.9.2 Oils (non volatile)

O-rings of cross section diameters 1.9, 2.6 and 5 mm and bore diameters 19, 20 and 21 mm respectively, designated S, M and L, were used as test pieces for immersion tests in approximately 10 times their weight of oil. The swelling was allowed to proceed in stoppered glass bottles placed in a fan-assisted air circulating oven at $100^\circ C$. The test piece was removed at intervals, weighed and reimmersed; initially at short intervals so that the penetration rate could be calculated. The time intervals were 2, 6, 24, 30, 48, 72 ... hrs. At equilibrium swelling the volumetric change was calculated as follows.

$$\Delta V = \frac{(W_5 - W_6) - (W_1 - W_2)}{(W_1 - W_2)} \times 100$$

$$\dots\dots\dots(58)$$

where W_1 = original weight of test piece in air
W_2 = original weight of test piece in liquid
W_5 = weight of swollen test piece in air
W_6 = weight of swollen test piece in liquid

To study the effect of soluble ingredients on the volume change, rings were extracted at room temperature with acetone and toluene and dried to constant weight. Immersion tests were then carried out in oils and the volumetric change ΔV_x of extracted samples has been calculated.

$$\Delta V_x = \frac{(W_7 - W_8) - (W_3 - W_4)}{(W_1 - W_2)} \times 100$$

$$\dots\dots\dots(59)$$

where $(W_7 - W_8)$ = volume of swollen ring (preextract)
$(W_3 - W_4)$ = volume of pre-extracted ring (dry)
$(W_1 - W_2)$ = original volume of ring

Note $(W_1 - W_2)$ = polymer + filler + extractables

$(W_3 - W_4)$ = polymer + filler

$(W_5 - W_6)$ = polymer + filler + liquid + extractables
less extractables removed by l.b.l.liquid

$(W_7 - W_8)$ = polymer + filler + liquid

$$\Delta V = \frac{\text{liquid volume} - \text{ingredients extracted by l.b.l. or oils}}{\text{polymer} + \text{filler} + \text{extractables}} \times 100 \quad (60)$$

$$\Delta V_x = \frac{\text{liquid volume}}{\text{polymer} + \text{filler} + \text{extractables}} \times 100 \quad (61)$$

$$\therefore \frac{\Delta V_x - \Delta V}{E_x} = \frac{E_x^1}{E_x} \times 100 \text{ (for oils)} = \% \text{ of acetone/toluene extractables extracted by oil.} \quad (62)$$

In certain instances, it is of interest to calculate the volume swelling ΔV_3 of the polymer in the mix. This obtained by multiplying ΔV by V_m the volume of mix which contains 100 volumes of polymer

$$\Delta V_3 = \frac{\Delta V \times V_m}{100}$$

2.10 The measurement of Swelling and Set under Compressive Strain

To study the effect of strain on the volume change and the percentage set, two compression set clamps were used to accommodate two sizes of test piece.

Clamp 1. This clamp consists of six circular (highly polished) steel plates 62 mm diameter. The upper and lower plates are 12 mm thick and the other four plates are 6 mm thick. Spacers, in the form of rings, around an axial bolt are placed between the plates to limit the degree of compression of the test pieces. The spacers used gave 10%, 15%, 25% and 40% compression. This clamp is shown in Fig. 2.2. Cylindrical test specimens approximately 13 mm in diameter and 6 mm thick were used, their thickness being accurately measured by means of a micrometer gauge.

Clamp 2. This clamp consists of four circular steel plates 112 mm in diameter. The upper and lower plates are 12 mm thick and the other two plates are 6 mm thick. Spacers in the form of broken rings around three bolts are placed between the plates.

Four axial circular small holes were made in the plates to permit oil to reach the inner diameter of the rubber O-rings M and L which were used in this clamp. (Fig. 2.3).

The following procedure was used in this test:-

a) the test pieces are placed between the plates after measuring their weights in air and in distilled water and their exact thicknesses.

b) the bolts are tightened uniformly until the plates are in contact with the spacers. Then the apparatus is immersed in oil and transferred to an oven.

c) After different time periods the clamp is parted and the excess oil on the surface of the test pieces is removed by blotting with filter paper. The test pieces are allowed to recover for 30 min.

d) Their thicknesses and weights are determined and they are then replaced between the plates, reclamped and reimmersed in oil.

This procedure is repeated until the sample has reached maximum swelling.

e) The difference between the original thickness of the test piece and that after recovery expressed as a percentage of the initially applied compression

$$= \% \text{ set } = \frac{h_o - h_r}{h_o - h_s} \times 100 \quad \ldots\ldots\ldots\ldots(63)$$

where h_o = the original thickness of the sample

h_r = the final thickness after recovery

h_s = the spacer thickness

This value can be used as a measure of the elasticity of the rubber, but, when carried out in oil, is affected by the

degree of swelling and penetration of the liquid into the rubber. A correction can then be made for the original thickness of the sample h_o by relating it to the percentage volume swell at equilibrium (under compressive strain) ΔV_s, then

$$h_e = h_o \left[1 + \frac{\Delta V_s}{100} \right]^{\frac{1}{3}} \qquad \dots\dots\dots\dots(64)$$

and the percentage set becomes $= \dfrac{h_e - h_r}{h_e - h_s} \times 100 \quad \dots(65)$

2.11 Experimental Error

It is essential to have estimates of the experimental errors associated with the various procedures and testing methods. These can be grouped as follows.

a. Mixing – including weighing and manipulating differences.

b. Vulcanisation – including unintentional variations of time and temperature.

c. Stress–strain relationship.

d. Swelling and extraction procedures. *one value of χ used for both NR & us.*

The stress–strain measurements can be considered to be extremely accurate and the only error arises from some difficulty in drawing the best lines through the points of the plot of f/A_0 v. $\lambda - \lambda^{-2}$ to arrive at the ratio $f/A_0(\lambda - \lambda^2)$.

The following experiments were carried out:-

1. duplicate batches of mix A_1 (Section 3) were prepared on different days.

2. duplicate vulcanisation of these two batches of mixes A_1 was carried out again on different days.

3. from each of the four vulcanised sheets, /replicate
   swelling and extraction measurements were made in
   toluene, to yield   the following results:-

Table 2.4 Statistical analysis of replicate swelling and

extraction measurements

*	Batch A		Batch B	
	Sheet i	Sheet ii	Sheet iii	Sheet iv
$\overline{\Delta V}_1$	178.5	182.7	188	188.8
σ	1.718	2.309	2.445	2.912
$C\nu$	.0096	.0126	.0130	.0154
$\overline{E}_x$	7.79	7.85	9.05	7.9
σ	.737	.303	0.710	.138
$C\nu$	.0946	.0385	.0785	.0175

* $\overline{\Delta V}_1$ is the mean swelling value, $\overline{E}_x$ mean extraction by volume. σ is the standard deviation and $C\nu$ coefficient of variation.(%)

It is possible now to calculate the mean values of swelling ΔV and E_x of the four batches, from which the standard deviation and coefficient of variation can be obtained. These values are as follows:

$$\overline{\Delta V} = 184.5 \quad \overline{E}_x = 8.15$$
$$\sigma = 4.794 \quad \sigma = 0.603$$
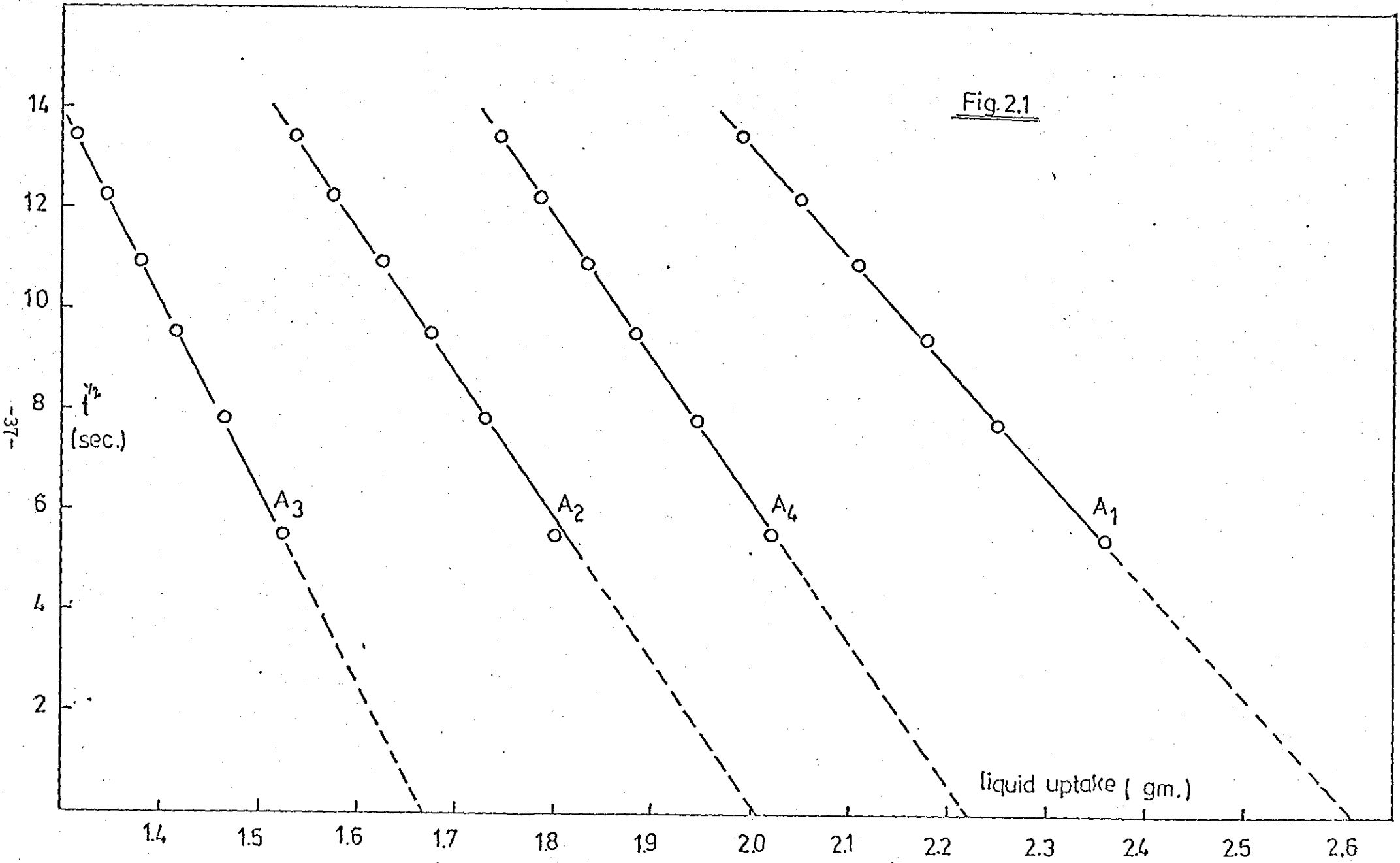$$C_\nu = .0250 \quad C_\nu = .0740$$

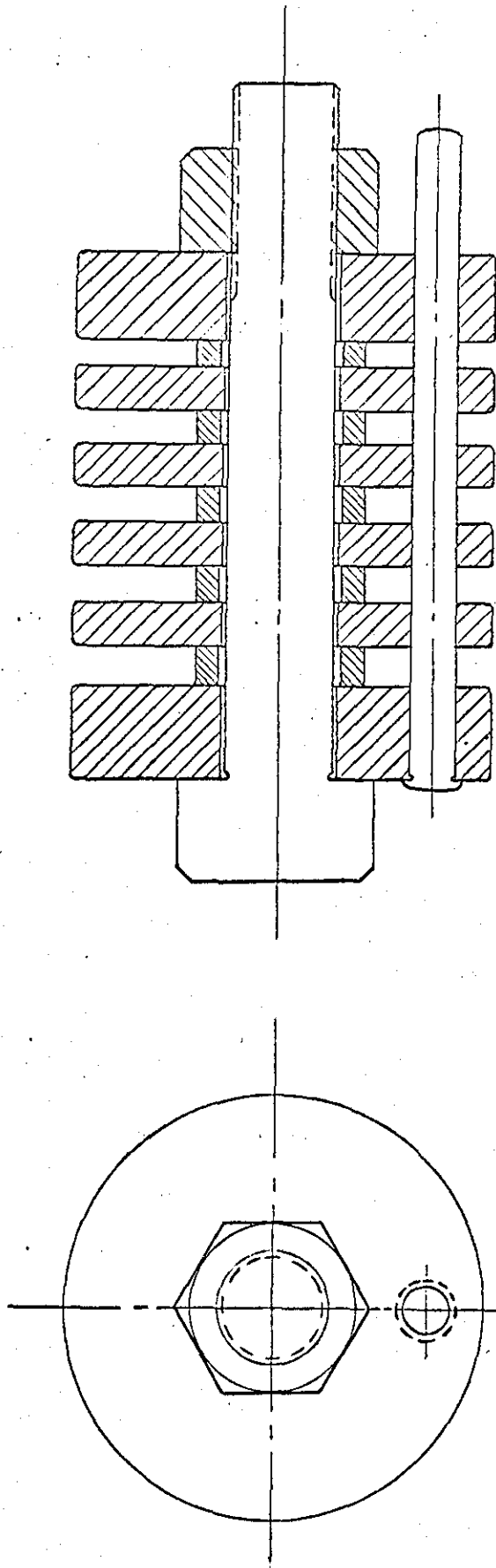Fig.2.1. Evaporation curves for Series A mix/chloroform.
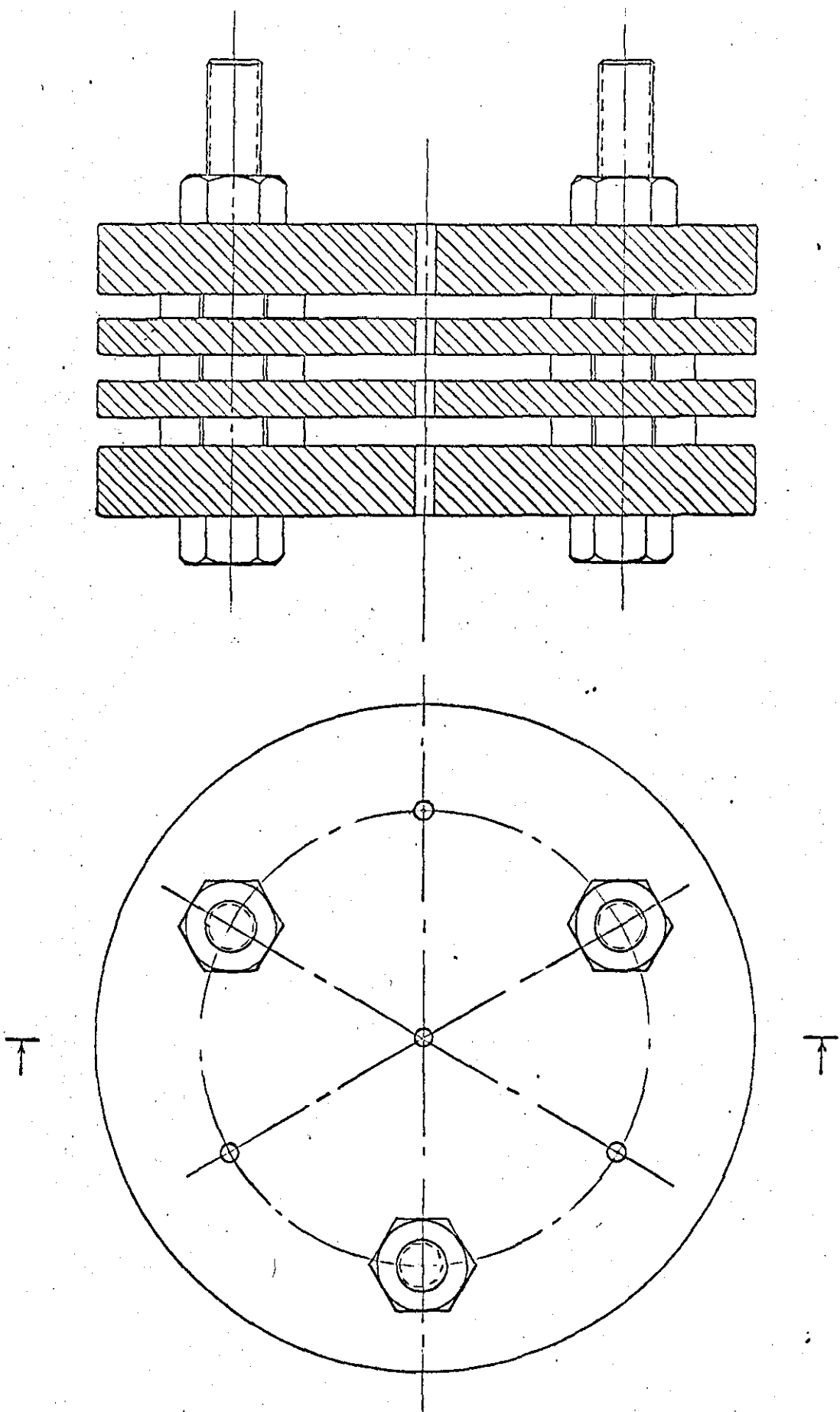
Fig.2.2 CLAMP 1

Fig.2.3   C LAMP 2

Section 3

Free Swelling Results

3.1 Introduction

In this section, the results of the free swelling experiments are given and are grouped in the several series of mixes in which, usually, only one factor has been varied, e.g. carbon black filler type, polymer content, cure system, cure time.

Rheometer, stress-strain and other physical data have been obtained on each series of mixes.

The stress-strain and volume change (in a range of liquids) results are recorded and some calculations and deductions reported but the detailed consideration of the interaction of the various results is deferred to the Discussion - section 4 .

3.2 Effect of Black type - Series A mixes

In this series of mixes, the basic formulation of which is given in Table 3.A.1., one polymer - 34.4% ACN content - has been employed; mix A_o is a pure gum mix and A_1-A_4 each contain an equal amount of four types of black; FT, SRF, FEF and HAF varying in particle size and structure.

The data from the Monsanto Rheometer on the unvulcanised mixes and the physical properties of the vulcanisates are given in Table 3.A.2. It is to be noted that hardness and stress at 100% show the expected increase with decrease of particle size, modified by the black structure factor.

Although the Monsanto Rheometer data suggested that 10 minutes at $150°C$ would be an adequate cure, in order to develop the best properties for oil swell and elasticity, 20 min was the cure time generally adopted.

The extractable contents of these five mixes are given in table 3.A.3; on average, there is no variation from mix to mix in the proportion of extractable solubles but toluene extracts 25% and chloroform 15% less than acetone.

In the case of the free swelling determinations of these mixes in low boiling liquids (l.b.l.) to equilibrium (Table 3.A.3.), the test pieces were dried to constant weight to obtain the amount extracted by solvents and, therefore, the amount of polymer in the swollen gel.

In figure 3.A.1., ΔV_1 is plotted against carbon black particle diameter for mixes A1-3 and shows a fair linear relationship.

For the free swelling determinations in non-volatile oils (stock 23) at 100°C, pre-extracted test pieces were used in addition to unextracted ones (Table 3.A.4.). The difference shows that only partial extraction of the solubles from the mixes by this oil has taken place.

In order to have data on the effect of cure time, samples of these mixes vulcanised 10, 30 and 40 minutes were subjected to swelling tests in another oil, Stock 27, at 100°C (Table 3.A.5). Also from these measurements, penetration rates were calculated in accordance with the equation. (2).

Equilibrium swelling is not significantly changed by change of cure time in this range but the penetration rates appear to increase with the particle size of the carbon black filler in the mix.

Stress-strain measurements were carried out in accordance with the method given in 2.5.3 ; The plot of f/A_0 against $\lambda - \lambda^{-2}$ is shown in figure 3.A.2 and the G values (section 2.5.3.) calculated are given in table 3.A.6. As is to be expected, G

Table 3.A.1. Series "A" mix formulations (Parts by weight)

Nitrile rubber (34.4 ACN)	100
Carbon black (see Table 3.A.2.)	50
Zinc oxide	5
Stearic acid	2
MC-sulphur	0.5
Cyclohexyl-benzthiazylsulphenamide (CBS)	1
Tetramethylthiuram disulphide (TMTD)	2
Antioxidant - OD	3

Table 3.A.2. Curemeter and vulcanisate properties. Series "A"

	A_1	A_2	A_3	A_4
Black type	FT	SRF	FEF	HAF
Particle size of black nm	180-200	70-95	39-55	28-36
Structure of black (cm^3 DBP/100g)	33	70	120	105
Minimum torque, Kgf cm	8	11.5	16.1	12.2
90% cure time, min	8.4	8.5	7.6	8
Torque value after 30 min, Kgf cm	79.4	101.2	110.4	98.9
Vulcanised 20 min at 150°C:				
Hardness, IRHD	56.5	64	67.7	68.5
Stress at 100% strain, Kgf/cm^2	11.3	34.0	(36.8)	38.0
Tensile strength, Kgf/cm^2	47.2	92.8	108.8	142
Elongation at break, %	320	235	180	220

Table 3.A.3. Percentage volume changes (ΔV_1), Extractable content percentage by volume (E_x) and v_r values for series "A" (rectangular test pieces cured 20 min at $150^\circ C$)

Mix No.	Acetone			Toluene			Chloroform			Hexane			Cyclohexane			n-heptane			n-Butanol			Formic acid		
	ΔV_1	E_x	v_r	ΔV_1	E_x	v_r	ΔV_1	E_x	v_r	ΔV_1	E_x	v_r	ΔV_1	E_x	v_r	ΔV_1	E_x	v_r	ΔV_1	E_x	v_r	ΔV_1	E_x	v_r
A_0	308	9.6	.2449	237	7.8	.2970	613	9.5	.1402	11.5	1.26	.8964	13.0	.99	.8852	9.4	1.5	.9141	38.5	4.2	.7222	49.5	5.1	.6690
A_1	223	6.9	.3099	180	4.5	.3566	426	5.8	.1901	9.0	.74	.9172	8.6	.94	.9209	4.5	.70	.9570	24.1	1.6	.8058	44.6	2.4	.6917
A_2	182	6.2	.3546	156	4.9	.3910	341	5.8	.2270	7.2	.77	.9330	8.2	.99	.9245	5.4	.95	.9489	21.8	1.4	.8213	40.0	2.4	.7144
A_3	165	6.6	.3778	147	5.0	.4040	267	5.3	.2726	6.0	.50	.9431	8.0	.45	.9255	4.0	.49	.9620	21.0	.7	.8266	38.1	2.2	.7243
A_4	186	7.0	.3495	161	5.6	.3838	332	4.7	.2315	9.2	.49	.9153	7.0	.22	.9343	3.9	.49	.9624	19.2	.5	.8391	40.1	1.9	.7137

Table 3.A.4. Series "A" Comparison data between ΔV (unextracted) and ΔV_x (extracted) - Stock 23 at $100^{\circ}C$. O ring-S vulcanised 10 min at $150^{\circ}C$

Mix No	$\Delta V_x - \Delta V$ %	E_x %	ΔV %	ΔV_x %
A_0	4.8	9.6	19.7	24.5
A_1	3.5	5.7	14.3	17.8
A_2	3.5	5.5	12.3	15.8
A_3	4.0	5.8	12.3	16.3
A_4	2.0	6.3	13.2	15.2

Table 3.A.5. % volume changes and penetration rates of series "A" mixes in oil stock 27 at $100^{\circ}C$. O-ring L test pieces vulcanised as indicated at $150^{\circ}C$

Mix No	% volume change			penetration rate $mm/hr^{\frac{1}{2}}$		
	10'	30'	40'	10'	30'	40'
A_1	5.0	5.3	5.3	.135	.131	.142
A_2	5.24	5.5	5.5	.124	.128	.139
A_3	5.2	5.4	5.4	.109	.121	.115
A_4	5.4	5.8	5.6	.117	.103	.124

Table 3.A.6. Comparison data between stress strain measurements G and corresponding values G' obtained from swelling

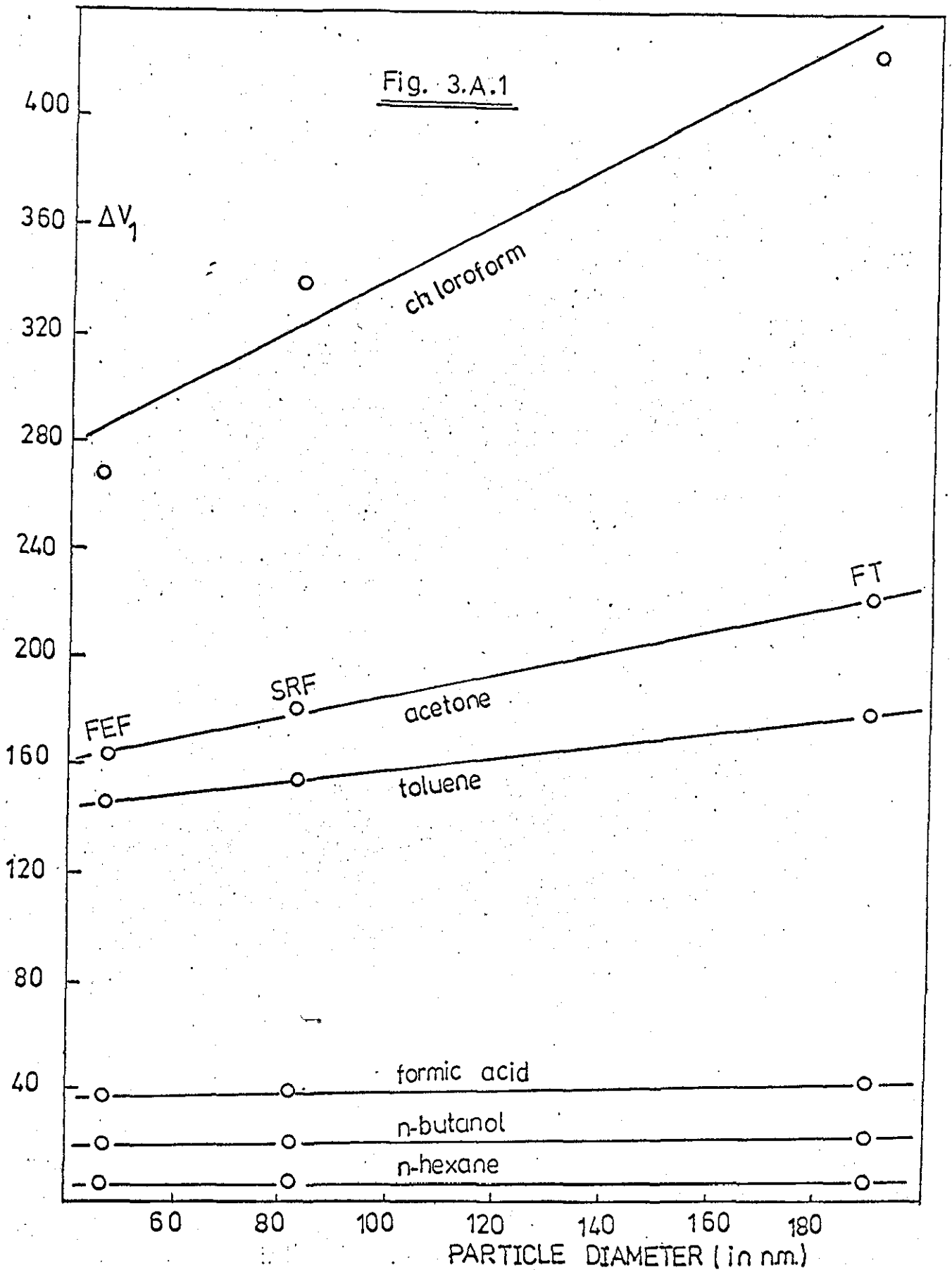| Mix No.	G	Acetone $\mu = .4617$		Toluene $\mu = .4830$		Chloroform $\mu = .1320$		Mean Value G'	G/G'
		v_r	G'	v_r	G'	v_r	G'		
A_0	4227	.2449	–	.2970	–	.1402	–		
A_1	3269	.3099	2192	.5366	2398	.1901	2330	2307	1.42
A_2	2207	.3546	1480	.3910	1790	.2270	1144	1471	1.50
A_3	1663	.3778	1231	.4040	1521	.2726	1111	1288	1.29
A_4	2163	.3495	1618	.3838	1898	.2315	1567	1694	1.28

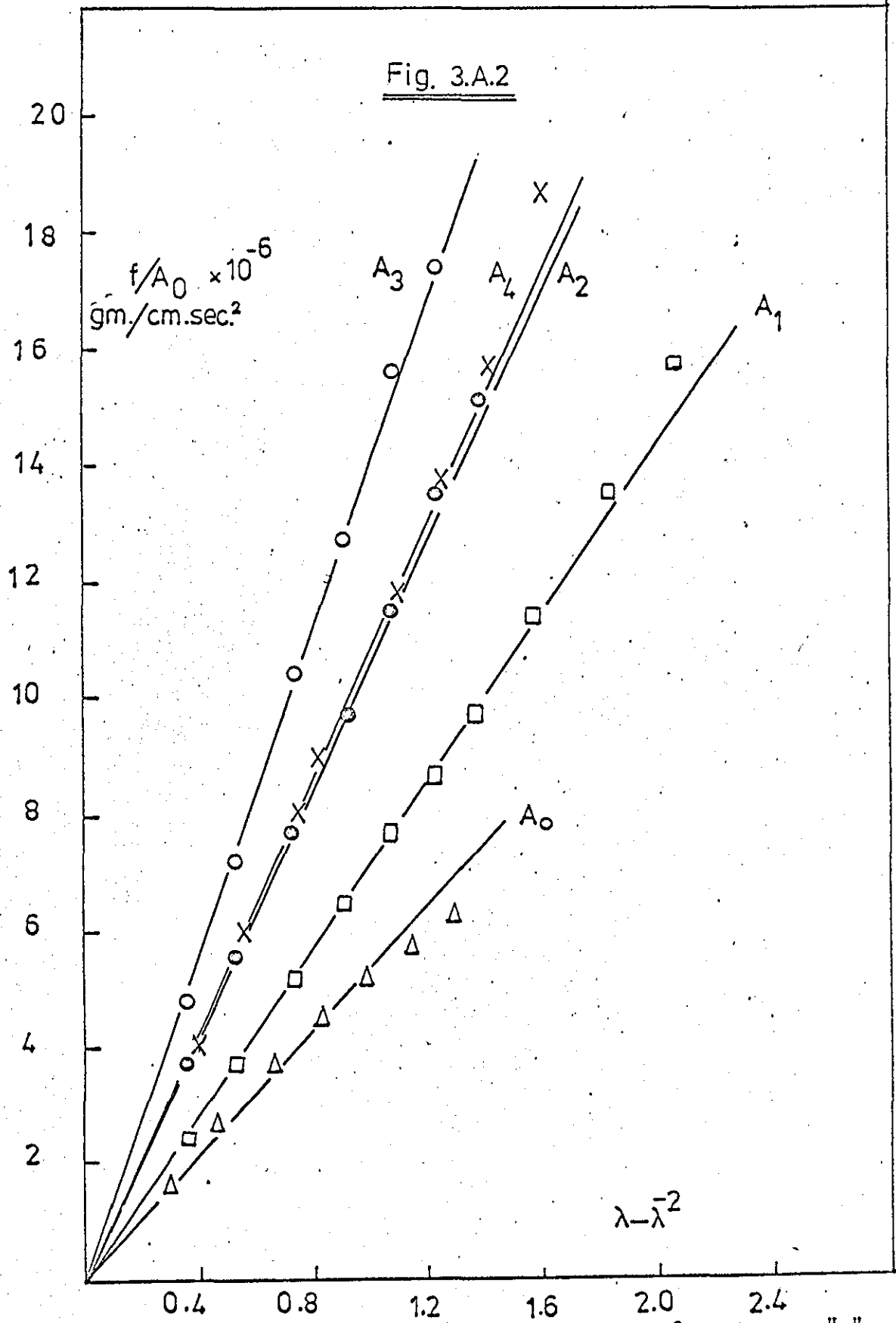Fig. 3.A.1. Relation between particle size diameter of carbon black and the percentage volume change ΔV_1

Fig. 3.A.2

Fig. 3. A. 2. Relation between f/A_0 and $\lambda - \bar{\lambda}^{-2}$ for series "A"
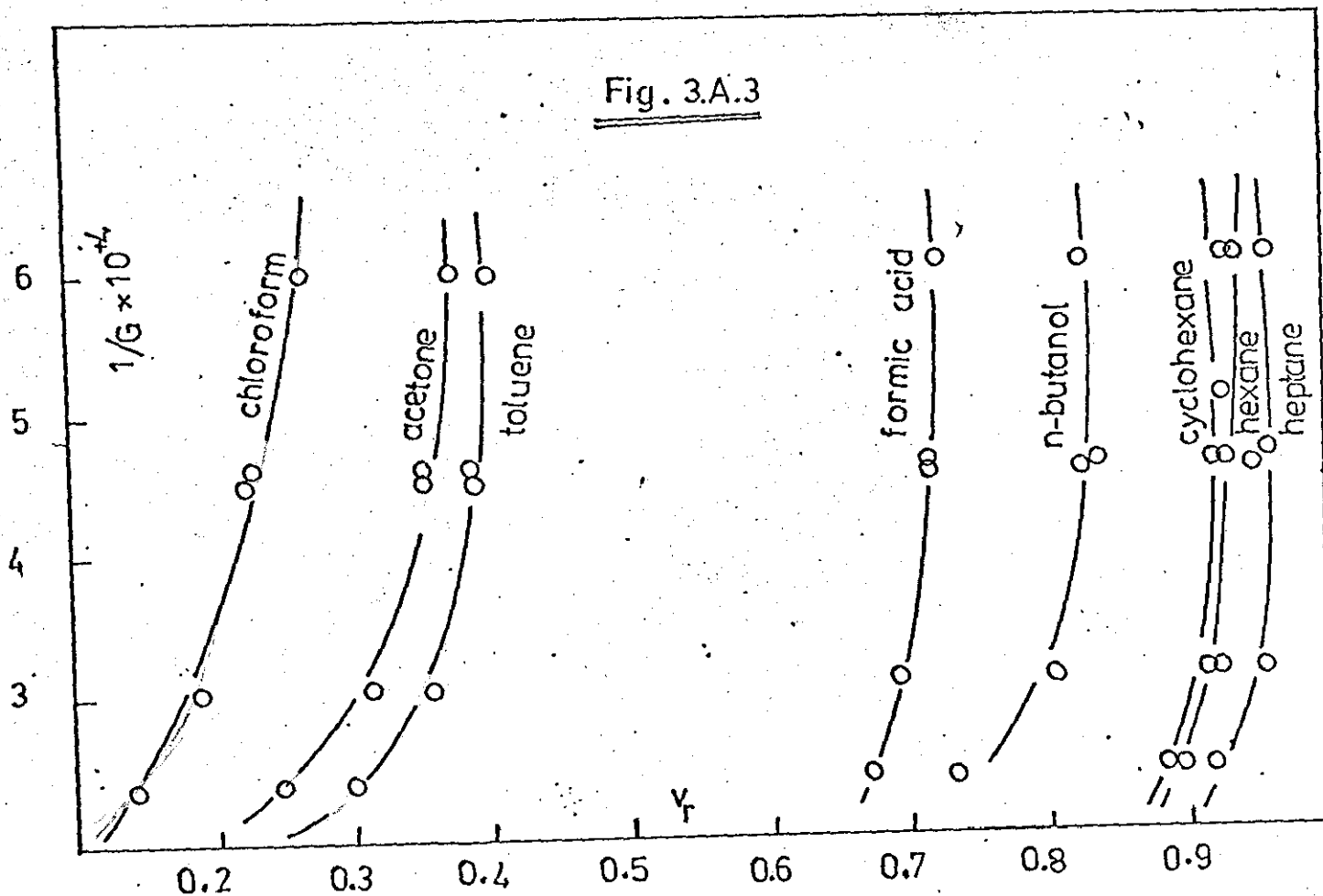
Fig. 3.A.3

Fig. 3.A.3. Relation between $1/G$ and v_r for Series "A" mix

varies with the black type employed in the compound. Further-
more, $1/G$ shows a good relationship to v_r for the liquid given
in Table 3.A.3. (Fig. 3.A.3.).

From the equilibrium swelling value and G on the pure gum
mix, A_o, the interaction constant μ, in equation (46) is
calculated (Table 3.A.6.), for several of the liquids which
produce a high degree of swelling.

Using these interaction constants and assuming they are
unaffected by the carbon black, values of G' are obtained for
the filled mixes Al-4 from the swelling results in the same
liquids using equation (46) (Table 3.A.6.).

For these latter calculations v_r has been taken as equal
to the volume fraction of polymer plus black (if present) in
the swollen gel in which the black is also included. Because
no attempt has been made to correct either G or G' for the filler
content, it is not surprising that these quantities differ from
black to black and G does not equal G'. However the ratio G /G'
is of interest.

3.3 Effect of polymer content – Series B mixes

In this series, the same basic formulation and polymer were
used as for the series A with the difference that the three
mixes Bl-3 contain different amounts of different blacks to
vary the polymer content and maintain approximately equal hardness
and modulus (Table 3.B.1.).

The data from the curemeter and the vulcanisate properties
are given in Table 3.B.2., and the extractable contents in
Table 3.B.3; 20 min cure time has generally been adopted as for
series A. Table 3.B.3. gives the results of free swelling
determinations in a range of low boiling liquids.

Table 3.B.1. Series B mix formulations (parts by weight)

	B₁	B₂	B₃
Nitrile rubber (34.4% ACN)	100	100	100
FT (black)	65	–	–
SRF (black)	–	35	–
HAF (black)	–	–	25
Zinc oxide	5	5	5
Stearic acid	2	2	2
MC-sulphur	0.5	0.5	0.5
CBS	1	1	1
TMTD	2	2	2
Antioxidant - OD	3	3	3

Table 3.B.2. Curemeter and vulcanisate properties

	B_1	B_2	B_3
Minimum torque Kgf cm	9.2	9.2	9.8
90% cure time, min	8.4	8.3	9.4
Torque value after 30 min Kgf cm	81.7	79.4	77.6
Vulcanised 20 min at 150°C:			
Hardness, IRHD	57	56	56.5
Stress at 100% strain, kg/cm²	14	26	20
Tensile strength, kg/cm²	64.4	74.0	80.8
Elongation at break, %	315	340	235

Table 3.B.3. Percentage volume change ΔV_1, Extractable content percentage by volume E_x and v_r values for series B mixes, rectangular test pieces cured 20 min at 150°C

Mix No.	Acetone			Toluene			Chloroform			Hexane			Cyclohexane			n-heptane			n-Butanol			Formic acid		
	ΔV_1	E_x	v_r	ΔV_1	E_x	v_r	ΔV_1	E_x	v_r	ΔV_1	E_x	v_r	ΔV_1	E_x	v_r	ΔV_1	E_x	v_r	ΔV_1	E_x	v_r	ΔV_1	E_x	v_r
Ao	308	9.6	.2449	237	7.8	.2970	613	9.5	.1402	11.5	1.26	.8964	13	.99	.8852	9.4	1.5	.9141	38.5	4.2	.7222	49.5	5.1	.6690
B_1	204	6.4	.3285	169	5.7	.3713	390	6.8	.2041	7.0	.5	.9346	8.7	.27	.9201	3.5	.55	.9665	21.5	2.2	.8231	46.7	2.7	.6817
B_2	223	7.6	.3096	181	6.1	.3565	403	7.7	.1989	7.0	1.0	.9348	11.9	.14	.8933	4.7	.60	.9549	24.9	2.5	.8008	47.3	2.8	.6789
B_3	241	8.0	.2932	193	6.8	.3417	441	7.7	.1849	7.4	.64	.9307	7.2	.31	.9326	5.2	.77	.9507	25.0	2.3	.8022	51.7	3.1	.6592

Table 3.B.4. Series B comparison data between ΔV_3 (unextracted) and ΔV_{3x} (extracted) – Stock 23 at 100°C. O ring-S vulcanised 20 min at 150°C

Mix No	$\Delta V_{3x} - \Delta V_3$ %	% Ex, by volume per 100V of polymer	ΔV_3 % per 100 of polymer	ΔV_{3x} % per 100 of polymer
Ao	4.8	9.6	19.7	24.5
B_1	4.8	9.0	19.2	24
B_2	4.0	9.5	17.8	21.8
B_3	4.3	8.9	19.4	23.7

Table 3.B.5. % volume change (ΔV) and penetration rate of Series B mixes in Stock 23 at 100°C. O ring-S test pieces vulcanised as indicated at 150°C

Mix No.	% volume change per 100 volume of mix				% volume change per 100 volume of polymer				Penetration rate mm/hr$^{\frac{1}{2}}$			
	10'	20'	30'	40'	10'	20'	30'	40'	10'	20'	30'	40'
B_1	13.2	13.9	14.6	14.6	19.2	20.2	21.2	21.2	.116	.121	.122	.121
B_2	13.9	14.8	14.6	15.8	17.8	19.0	19.0	20.3	.144	.144	.152	.153
B_3	15.8	16.6	16.6	16.6	19.4	20.4	20.4	20.4	.158	.172	.172	.172

Table 3.B.6. Comparison data between stress-strain measurements G and corresponding values obtained from swelling

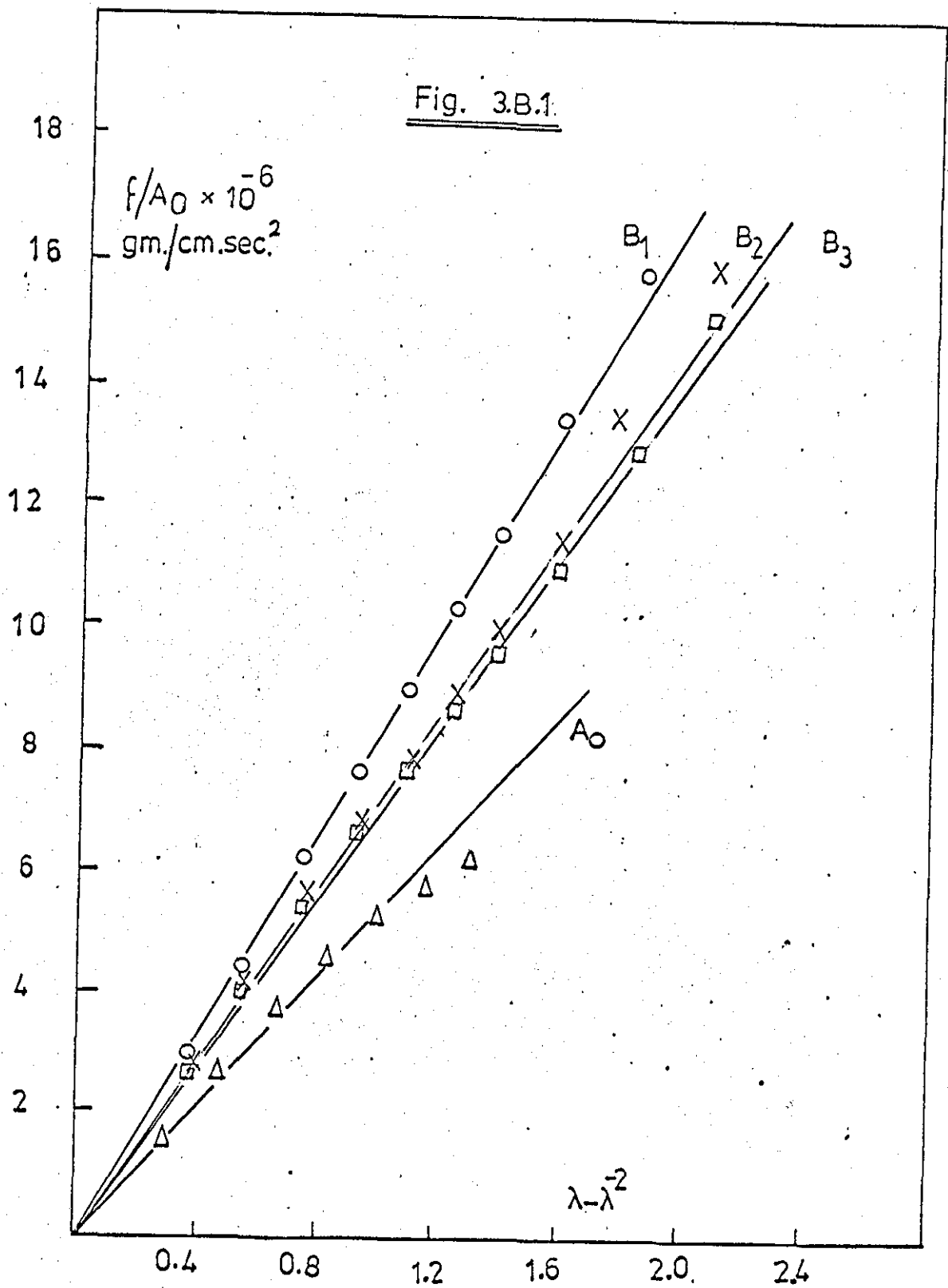| Mix No.	G	Acetone $\mu = .4617$		Toluene $\mu = .4830$		Chloroform $\mu = .1320$		Mean Value G'	G'/G
		v_r	G'	v_r	G'	v_r	G'		
Ao	4227	.2449	–	.2970	–	.1402	–	–	–
B_1	2842	.3285	1856	.3713	2115	.2041	2021	1997	1.42
B_2	3274	.3096	2205	.3565	2411	.1989	2125	2247	1.46
B_3	3369	.2932	2594	.3417	2746	.1849	2455	2598	1.30

Fig. 3.B.1. Relation between f/A_0 and $\lambda - \lambda^{-2}$ for series "B"

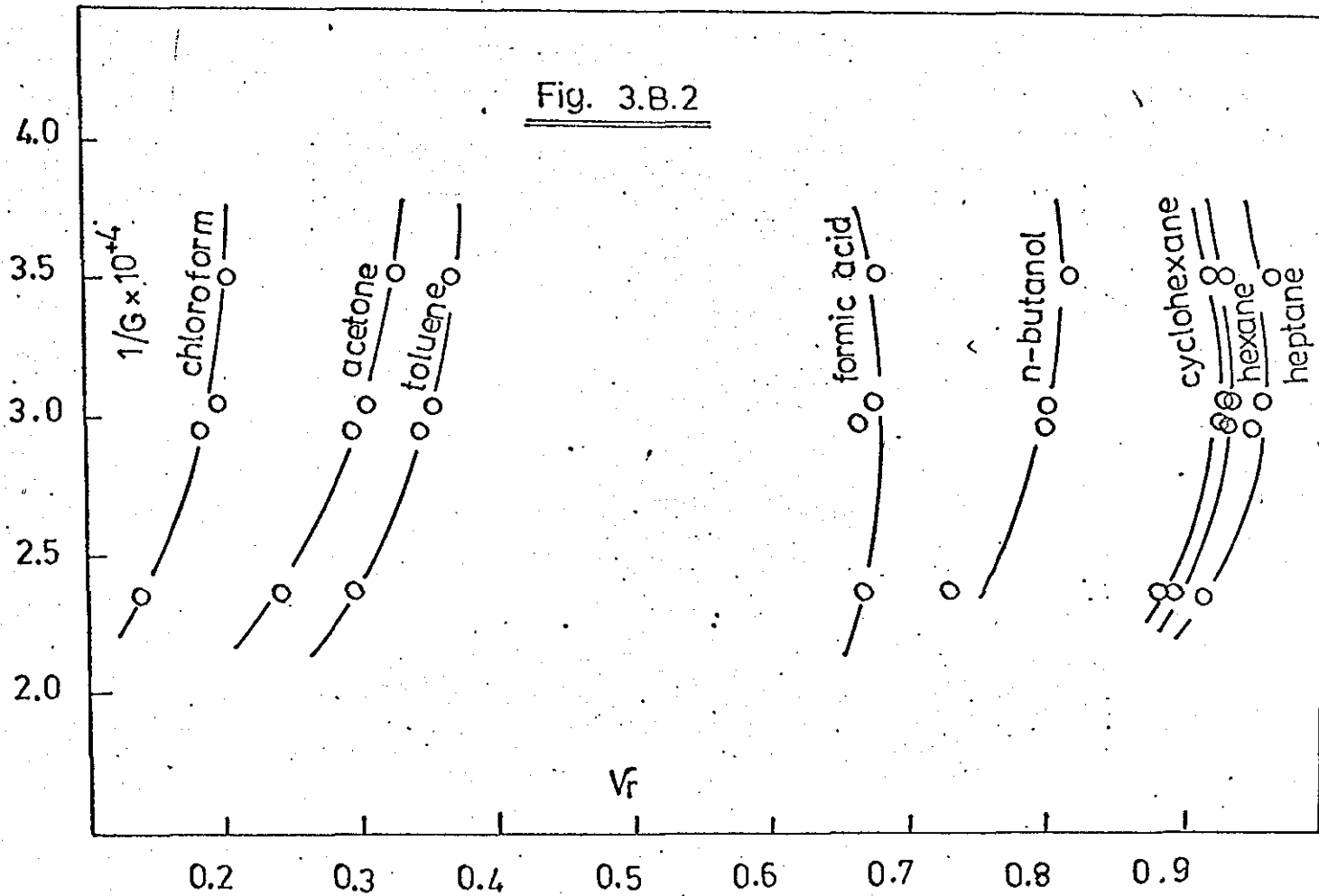Fig. 3.B.2. Relation between 1/G and v_r for Series "B" mix.

Table 3.B.4., the results of swelling in oil - stock 23.

A range of cure times was also carried out with results, in Table 3.B.5., showing a slightly greater sensitivity to cure time and a similar penetration rate increase with cure time to that shown by series A. The explanation of the increase of penetration rate in going from B_1 to B_2 to B_3 may lie in the lower filler content.

This series has been treated in a similar manner; stress-strain determinations yielded the values of G Fig. 3.B.1.; μ values already obtained for A_o have been used to calculate G' and G/G' (Table 3.B.6.). Figure 3.B.2. shows the relation of $1/G$ to v_r for these mixes in the solvents Table 3.B.4.

3.4 Effect of cure system - Series C mixes

So far cure time and cure system have been kept constant and furthermore only one polymer has been used. This has meant that one value for μ for each liquid could be used throughout. In order to extend the applicability of the scheme to be proposed later, it is essential to study firstly the effect of cure system (i.e. recipe) and secondly cure time and thirdly the effect of acrylonitrile content variation on the value of μ.

In this series C, the same polymer has been used and a constant level of 100 parts by weight of FT black. The curing systems are as given in Table 3.C.1. and the Rheometer results and vulcanisate properties in Table 3.C.2. The effect of varying the cure system has been to vary the time to optimum cure as indicated. For the vulcanisate properties reported in Table 3.C.2., the cure time was 20 min and this explains in part the lower

modulus of C_3. The extractable contents in Table 3.C.5. show a wider range of values as is to be expected.

It is to be noted that mix C_4 has the same cure system as mixes A_1 and B_1 and the same type of carbon black filler, ie.FT; the proportions being 100, 50 and 65 respectively. Table 3.C.3. gives the data for C_4 mix with the three solvents. A comparison can then be made between G and $\acute{G}$ for these three mixes, alongside Ao which is the gum mix of the same base composition.

Table 3.C.4. gives the data from which it is seen that the $\acute{G}/G$ ratio is constant to within $\pm$ .03.

The same procedure has been adopted as for series A and B. Table 3.C.5. gives the results of free swelling determinations in a range of low boiling liquids. Figure 3.C.1. shows the relation of $1/G$ to v_r for three mixes in the solvents. Table 3.C.6. the results for swelling in oil stock 23 at $100^{\circ}C$. Once again extraction of ingredients from the rubber by the oil has been incomplete.

Table 3.C.7. gives the results of a series of cure times; from these it is concluded that over the range studied both equilibrium volume change and penetration rate are little affected by the cure time, in the case of liquids with low swelling power towards the particular polymer.

Using the same interaction constant and assuming it is the same for each cure system, $\acute{G}$ values can be obtained for C_1-C_3 and the $G/\acute{G}$ ratio. This ratio is 1.42 $\pm$ .07 and means that the above assumption is true; Table 3.C.8.

Table 3.C.1. Series C mix formulation (parts by weight)

	c_1	c_2	c_3	c_4
Nitrile rubber (34.4 ACN)	100	100	100	100
FT (black)	100	100	100	100
Zinc oxide	5	5	5	5
Stearic acid	2	2	2	2
Sulphur	2.5	.35	-	0.5
MBT	1.0	-	-	-
CBS	-	1.4	-	1.0
TMTD	-	.66	3.0	2.0
Antioxidant - OD	3.0	3.0	3.0	3.0

Table 3.C.2. Curemeter and vulcanisate properties "C" series

	c_1	c_2	c_3	c_4
Minimum torque, Kgf cm	7.5	11.5	8.9	9.2
90% cure time min	11.5	8	23.0	10
Torque value after 30 min, Kgf cm	85.1	69	62.1	47.2
Vulcanised 20 min at 150°C				
Hardness, IRHD	64	59	56	65
Stress at 100% strain, kg/cm^2	32	16	12	24
Tensile strength, kg/cm^2	76	70.8	76	64
Elongation at break, %	410	465	580	305

Table 3.C.3. Comparison data between stress-strain measurement G and corresponding value $\tilde{G}'$ obtained from swelling for C_4 mix, rectangular samples 20 min cure at $150^{\circ}C$

Mix No.	G	Acetone $\mu = .4617$		Toluene $\mu = .4830$		Chloroform $\mu = .1320$		Mean Value G'	G'/G
		v_r	G'	v_r	G'	v_r	G'		
C_4	2395	.3481	1570	.4013	1646	.2251	1659	1625	1.47

Table 3.C.4. Effect of FT carbon black amount on the G and G' value

	A_o	A_1	B_1	C_4
C-black parts by wt per 100 parts of polymer	0	50	65	100
Volume fraction of carbon black	0	.213	.296	.352
G' value obtained from swelling	–	2307	1997	1628
G value obtained from stress-strain	4227	3269	2842	2395
G/G'	–	1.42	1.42	1.47

Table 3.C.5. Percentage volume ΔV_1, Extractable content percentage by volume E_x and v_r values for series A, rectangular test pieces cured 20 min at $150^{\circ}C$.

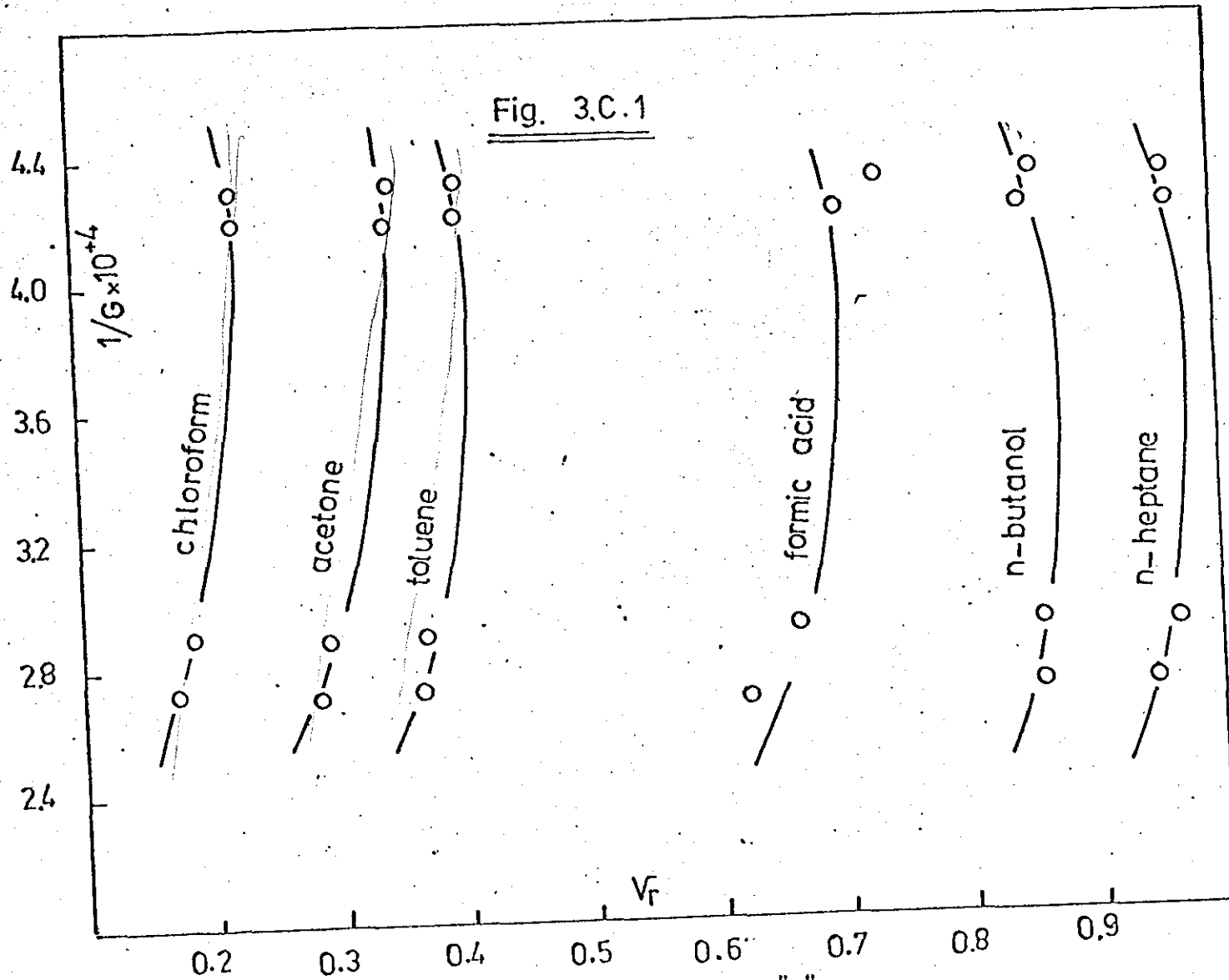| Mix No.	Acetone			Toluene			Chloroform			n-Heptane			n-Butanol			Formic acid		
	ΔV_1	E_x	v_r	ΔV_1	E_x	v_r	ΔV_1	E_x	v_r	ΔV_1	E_x	v_r	ΔV_1	E_x	v_r	ΔV_1	E_x	v_r
C_1	183	4.0	.3539	142	3.0	.4135	346	4.1	.2244	3.7	-	.9641	15.5	.25	.8654	34.9	1.8	.7415
C_2	238	5.1	.2960	171	5.5	.3685	438	6.2	.1858	3.4	-	.9671	24.0	.7	.8063	49.9	2.1	.6671
C_3	244	6.1	.2904	182	5.6	.3549	495	6.9	.1680	5.4	.3	.9485	23.1	1.2	.8125	61.5	3.4	.6189
C_4	187	5.1	.3481	149	4.4	.4013	344	5.5	.2251	3.8	-	.9635	18.5	1.3	.8438	41.8	2.0	.7053

Fig. 3.C.1 Relation between 1/G and v_r for Series "C" mix

Table 3.C.6. Series C comparison data between ΔV (unextracted) and ΔV_x extracted. Stock 23 at 100°c.O-ring-S vulcanised 20 min at 150°C

Mix No.	$\Delta V_x - \Delta V$ %	% E_x	ΔV %	ΔV_x %
C_1	1.8	3.5	10.9	12.8
C_2	2.4	5.3	11.0	13.4
C_3	2.9	5.8	11.4	14.3
C_4	4.0	4.7	9.6	13.6

Table 3.C.7. % volume changes and penetration rates of series C mixes in stock 27 oil at 100°C, O ring-L test pieces vulcanised as indicated at 150°C

Mix No.	% Volume change					Penetration rate mm/hr$^{\frac{1}{2}}$				
	10'	20'	30'	50'	70'	10'	20'	30'	50'	70'
C_1	4.5	4.5	4.5	4.4	4.4	.125	.121	.120	.121	.123
C_2	5.5	5.5	5.4	5.7	5.3	.126	.127	.118	.118	.114
C_3	4.8	4.8	4.8	4.9	4.9	.121	.123	.119	.130	.127
C_4	4.5	4.5	4.5	4.5	4.6	.124	.131	.124	.128	.131

Table 3.C.8. Comparison data between stress-strain measurements G and G' corresponding values/obtained from swelling

Mix No.	G	Acetone $\mu = .4617$		Toluene $\mu = .4830$		Chloroform $\mu = .1320$		Mean Value G'	G/G'
		v_r	G'	v_r	G'	v_r	G'		
C_1	2321	.3539	1492	.4135	1492	.2244	1673	1556	1.49
C_2	3465	.2960	2498	.3685	2154	.1858	2441	2364	1.46
C_3	3685	.2904	2715	.3549	2464	.1680	2978	2719	1.35

3.5 Effect of cure time – Mix D

Ranges of cure times for several of above series were investigated. In the majority of cases the volume swelling in oils and low boiling liquids was little influenced by cure time. Mix D based on a low acrylonitrile content polymer (20% ACN), otherwise the same composition as A_1 mix, (i.e. 50 phr of FT black) is selected to show this effect. Table 3.D.1. gives the extractable contents by volume. Table 3.D.1. gives also the results of free swelling determinations in acetone, toluene and chloroform. Table 3.D.2. the results of free swelling in oil Stock 23. It is to be noted from these tables that the swelling and extraction data for the l.b.l. and the stress strain G value at the four cure times, 10, 20, 30 and 40 mins are not very significantly affected. The small progressive change in G at constant v_r will give difference in µ but this is comparatively very small.

From the equilibrium swelling value and G on the pure gum mix Do, the interaction constant µ in equation (46) was calculated. This interaction constant was used to calculated G' for mix D at 20' cure using swelling results from the same liquids and the G/G' ratio was calculated (Table 3.D.3.)

Although the polymer used in this mix is different from that used in series A, B, and C, the ratio G/G' still has the same value (1.42).

3.6 Effect of acrylonitrile content – Series L mixes

So far, the G/G' ratios of mixes D and A_1, based on two polymers of different ACN content, i.e. 20% and 34.4% have the same value; it appeared of interest then to observe this ratio for an extended range of acrylonitrile content polymers.

Table 3.D.1. Percentage volume change ΔV_1 and Extractable content percentage by volume E_x for mix D vulcanised at $150^\circ C$.

Cure time	Acetone		Toluene		Chloroform		G
	ΔV_1	E_x	ΔV_1	E_x	ΔV_1	E_x	
10'	144	8.3	328	9.0	539	9.6	2246
20'	144	8.4	326	8.7	530	9.4	2222
30'	143	8.3	326	8.7	533	9.6	2104
40'	143	7.9	326	9.2	531	9.3	2048

Table 3.D.2. Mix "D" Comparison data between ΔV (unextracted and ΔV_x (extracted) - Stock 23 at $100^\circ C$ - 0 ring M vulcanised at $150^\circ C$.

Cure time	$\Delta V_{x\%} - \Delta V$	$E_{x\%}$	$\Delta V_\%$	$\Delta V_{x\%}$
10'	17.2	9.0	43.6	60.8
20'	14.5	8.8	42.8	57.3
30'	14.0	8.8	42.8	56.8
40'	14.5	8.8	42.7	57.2

Table 3.D.3. Comparison data between stress-strain measurements G and corresponding values G' obtained from swelling; Mix D at 20' cure time.

Mix No.	G	Acetone $\mu = 0.601$		Toluene $\mu = 0.190$		Chloroform $\mu = 0.0123$		Mean G'	G/G'
		v_r	G'	v_r	G'	v_r	G'		
D_o	3 922	0.3702	–	0.1921	–	.1274	–	–	–
D	3111	0.4115	2106	0.2347	2183	.1585	2273	2187	1.42

In this series, three other polymers of 27.3, 40.7 and 44.1%
denoted as L_1, L_3 and L_4,
acrylonitrile content/have been used and a constant level of 100

parts by weight of FT black and the same cure system as A_1 and D.

Mix C4 forms a fourth in this series, having 100 parts of FT

black and the same cure system.

                            the
The data from the curemeter and/ vulcanisate properties are

given in Table 3.L.1., and extractable contents in Table 3.L.2.;

20 min cure time has adopted for series L. Table 3.L.3. gives

the results of free swelling in the three low boiling liquids;

acetone, toluene and chloroform; Table 3.L.3. the results of

swelling in oil stock 23. It is also noticed from these results

that only partial extraction has taken place.

A series of cure times was also carried out in this series,

Table 3.L.4. showing a small change with cure time; the volume

change and penetration rate decrease with the increase of the

acrylonitrile content in the polymer.

To calculate the interaction constant for these polymers,

free swelling determinations, in a range of l.b.ls., and stress

strain measurements have been carried out on pure gum mixes of

the same basic formulation, denoted as L_{01}, L_{02}, L_{03}, L_{04}.

Table 3.L.5. gives the results of free swelling determinations in

a range of l.b.l's and Table 3.L.6. the polymer-solvent inter-

action constant μ. Included in these 2 tables are mixes D_o and E_o,

the latter being based on a sixth polymer of ACN content 27.8[*].

An interesting plot of μ as a function of the acrylonitrile

content is shown in Fig. 3.L.1, μ and v_r values relating to

[*] For completeness, these tables include data previously given

in Tables 3.D.1. and 3.E3.

eight l.b.l. and pure gum mixes based on the six polymers are plotted in Fig. 3.L.2.

Using these interaction constants and assuming they are unaffected by carbon black, G' values were obtained for the filled rubbers L_{1-3} from swelling results in the same solvents. Table 3.L.7. In the same table, the G values obtained by stress-strain measurements and the G/G' values are tabulated.

Results given in Table 3.L.6. have been used to construct the Bristow and Watson plot of the solubility parameter of the l.b.ls "δ_1" against the value $\delta_1^2/RT - \mu/V$ given in equation (50). Good straight lines were obtained as suggested by this equation. From the slope of these lines the solubility parameters "δ_2" of the polymers were found. Fig. 3.L.3.

In order to find out δ_2 from the intercept of these lines, it is desirable to find out the constant value μ_s.

This constant was obtained from the previous experimental results in which $\mu = .483$, (L_2 - toluene) and $\delta_2 = 9.9$ (for L_2 using Fig. 3.L.3.) in equation (50). This value for μ_s is equal to 0.30. Table 3.L.8. gives values for δ_2 obtained from both slope and intercept (using the value 0.3 for μ_s) and shows that μ_s is substantially constant for this series. It is to be noted from this table that the solubility parameter increases with increasing the acrylonitrile content; see also Fig. 3.L.4.

Table 3.L.1 Curemeter and vulcanizate properties of L series

	L_1	$L_2=C_4$	L_3	L_4
Minimum torque, Kgf cm	15.2	11.27	10.9	9.4
90% cure time min	7.4	7.2	7.6	7.7
Torque value after 30 min, Kgf cm	107.4	101.0	83.4	83.4
vulcanized 20 min at 150°C:				
Hardness,IRHD	68	66	66.5	72.5
Stress at 100 strain, kg/cm^2	12.8	14.0	14.0	17
Tensile strength, kg/cm^2	66.4	68.4	62.0	57.2
Elongation at break,%	420	420	440	410

Table 3.L.2. Percentage volume change ΔV_1, Extractable content percentage by volume (E_x) and v_r values for series L - rectangular test pieces cured 20' at 150°C.

Mix No.	Acetone			Toluene			Chloroform		
	ΔV_1	E_x	v_r	ΔV_1	E_x	v_r	ΔV_1	E_x	v_r
L_1	157	4.7	.3891	196	5.0	.3378	357	5	.2188
L_2	187	5.9	.3481	149	5.1	.4013	344	6.4	.2251
L_3	193	5.4	.3413	110	4.9	.4762	378	5.8	.2092
L_4	202	5.7	.3305	95	3.6	.5129	389	6.5	.2045

Table 3.L.3. L-series comparison data between ΔV (unextracted) and ΔV_x (extracted) - stock 23 at 100°C - 0 rings-S vulçanized 20' at 150°C

Mix No	$\Delta V_x - \Delta V$ %	$E_x c \backslash^{0}$	ΔV %	ΔV_{x} %
L_1	4.9	4.9	21.8	26.7
$L_2 = C_4$	3.1	5.5	11.4	14.5
L_3	1.8	5.5	7.6	9.4
L_4	0.8	5.3	4.9	5.7

Table 3.L.4. % volume change (ΔV) and penetration rate of series L mixes in oil stock 23 at 100°C. 0 ring-S test pieces vulcanized as indicated at 150°C.

Mix No.	% volume change				Penetration rate mm/hr$^{\frac{1}{2}}$			
	10'	20'	30'	40'	10'	20'	30'	40'
L_1	20.9	21.8	21.8	21.8	.212	.215	.211	.215
$L_2 = C_4$	11.35	11.35	11.35	11.5	.098	.098	.098	.097
L_3	7.5	7.5	7.5	7.5	.054	.054	.046	.039
L_4	3.9	4.9	4.9	5.5	.032	.032	.032	.032

Table 3.L.5. Percentage volume change ΔV_1, Extractable content percentage by volume E_x and v_r' values for series L mixes - rectangular test pieces cured 20 min at $150\,^{\circ}C$ (pure gum)

Mix No.	Acetone			Toluene			Chloroform			Hexane			Cyclohexane			n-heptane			n-butanol			Formic acid		
	ΔV_1	E_x	v_r	ΔV_1	E_x	v_r	ΔV_1	E_x	v_r	ΔV_1	E_x	v_r	ΔV_1	E_x	v_r	ΔV_1	E_x	v_r	ΔV_1	E_x	v_r	ΔV_1	E_x	v_r
D_0	170	10.4	.3702	421	12	.1921	685	13.7	.1274	31.5	6.4	.1605	76.5	8.7	.5684	30.6	7.6	.7658	29.5	7.6	.7722	34.8	1.32	.7418
L_{01}	230	9.5	.3028	332	9.2	.2316	725	10.2	.1323	20.5	3.0	.8299	43.6	4.9	.6964	19.3	4.2	.8382	34.5	6.4	.7435	49.8	1.76	.6675
E_0	234.4	6.1	.2990	327.2	5.0	.2341	436.1	9.2	.1865	19.7	2.0	.8354	44.7	2.6	.6911	17.9	1.4	.8482	27.2	2.9	.7862	43.2	1.70	.6982
$L_{02}=A_0$	308	9.6	.2449	237	7.8	.2970	613	9.5	.1402	11.5	1.26	.8964	13	.99	.8552	9.4	1.5	.9141	38.5	4.2	.7222	49.5	5.1	.6690
L_{03}	356	14.7	.2192	169	8.7	.3722	656	10.9	.1183	4.6	1.4	.9550	4.0	.42	.9617	3.4	1.2	.9672	22.5	3.5	.8160	86.9	6.07	.5350
L_{04}	376	9.6	.2099	143	7.4	.4123	745	10.9	.1208	2.5	0.7	.9756	2.5	.35	.9755	1.5	1.0	.9854	19.5	2.2	.8368	110.0	11.55	.4762

Table 3.L.6. Interaction constant for the different polymers (pure gum)

Mix No.	ACN	G	Acetone		Toluene		Chloroform		Hexane		Cyclohexane		n-heptane		n-butanol		Formic acid	
			V_r	μ	V_r	μ	V_r	μ	V_r	μ	V_r	μ	V_r	μ	V_r	μ	V_r	μ
D_0	20	3922	.3702	.601	.1921	.190	.1274	.012	.7605	1.129	.5664	.797	.7658	1.139	.7722	1.167	.7418	1.104
L_{01}	27.3	3611	.3028	.530	.2316	.373	.1323	.046	.8299	1.341	.6964	.989	.8382	1.371	.7435	1.093	.6675	.961
E_0	27.8	4700	.2990	.543	.2341	.394	.1865	.345	.8354	1.377	.6911	.7791	.8482	1.420	.7862	1.208	.6982	1.023
$L_{02}=A_0$	34.4	4227	.2449	.462	.2970	.483	.1402	.132	.8964	1.687	.8552	1.616	.9141	1.823	.7222	1.050	.6690	.965
L_{03}	40.7	4548	.2192	.435	.3722	.588	.1183	.029	.9560	2.358	.9617	2.476	.9672	2.604	.8160	1.002	.5350	.804
L_{04}	44.1	4305	.2099	.419	.4123	.635	.1208	.079	.9756	2.860	.9755	2.859	.9854	3.321	.8368	1.364	.4712	.731

Table 3.L.7. Comparison data between stress-strain measurements G and corresponding values G' obtained from swelling for L series.

Mix No.	Amount of C.Black (parts by weight)	G	Acetone			Toluene			Chloroform			G'	G/G'
			μ	v_r	G'	μ	v_r	G'	μ	v_r	G'		
D_0	50	3111	.601	.4115	2106	.190	.2347	2183	.0123	.1585	2273	2187	1.42
L_1	100	2147	.530	.3891	1608	.373	.3378	1588	.0457	.2188	1479	1558	1.38
L_2	100	2395	.462	.3481	1570	.483	.4013	1646	.132	.2251	1659	1625	1.47
L_3	100	2274	.435	.3413	1492	.588	.4762	1552	.029	.2092	1602	1549	1.47
L_4	100	2319	.419	.3305	1516	.635	.5129	1465	.079	.2045	.1838	1606	1.44

Table 3.L.8. Solubility parameter for the six polymers used

Mix No	ACN	Solubility parameter δ_2 from:	
		Slope	Intercept
D_0	20.0	9.19	9.22
L_{01}	27.3	9.66	9.63
E_0	27.8	9.65	9.61
L_{02}	34.4	9.86	9.90
L_{03}	40.7	10.30	10.31
L_{04}	44.1	10.57	10.57
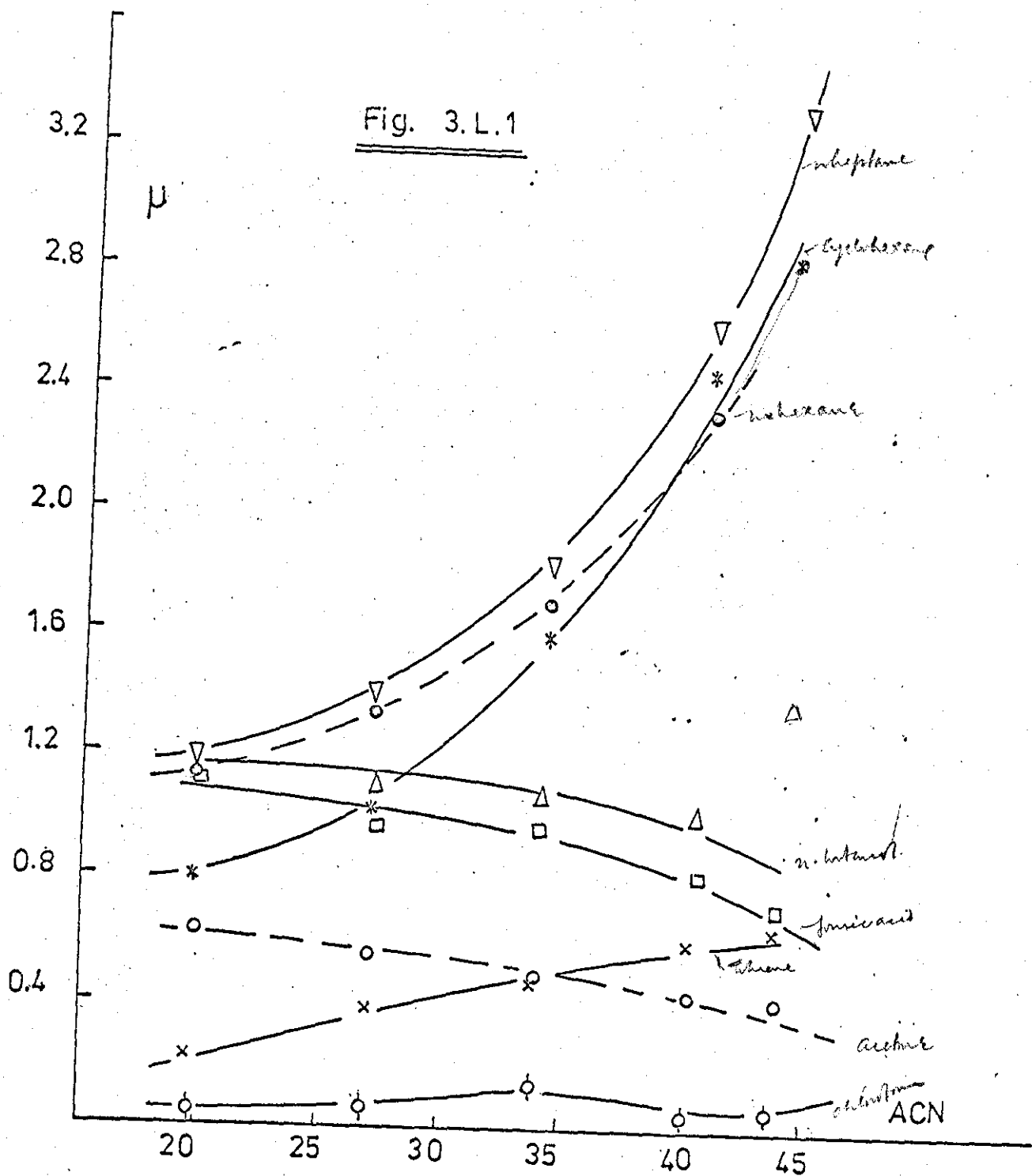
Fig. 3L.1 Relation between the interaction constant μ and ACN : O Acetone
×Toluene , ⌀ Chloroform , ⊙ n Hexane ∇ n Heptane,✳Cyclohexane , △ n Butanol,
□ Formic acid.
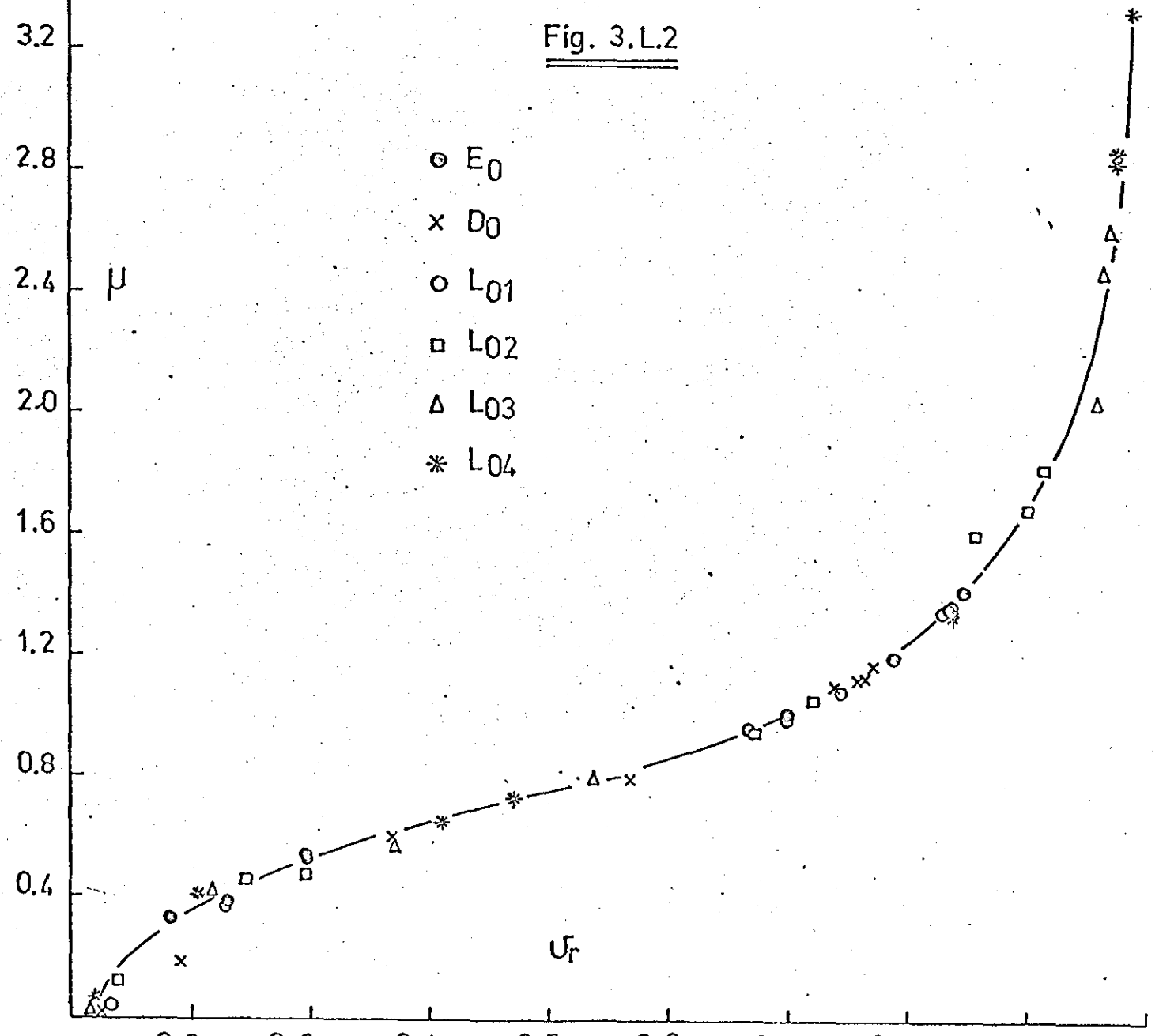
Fig. 3.L.2

Fig. 3.L.2 Relation between the interaction constant and v_r. (liquids)
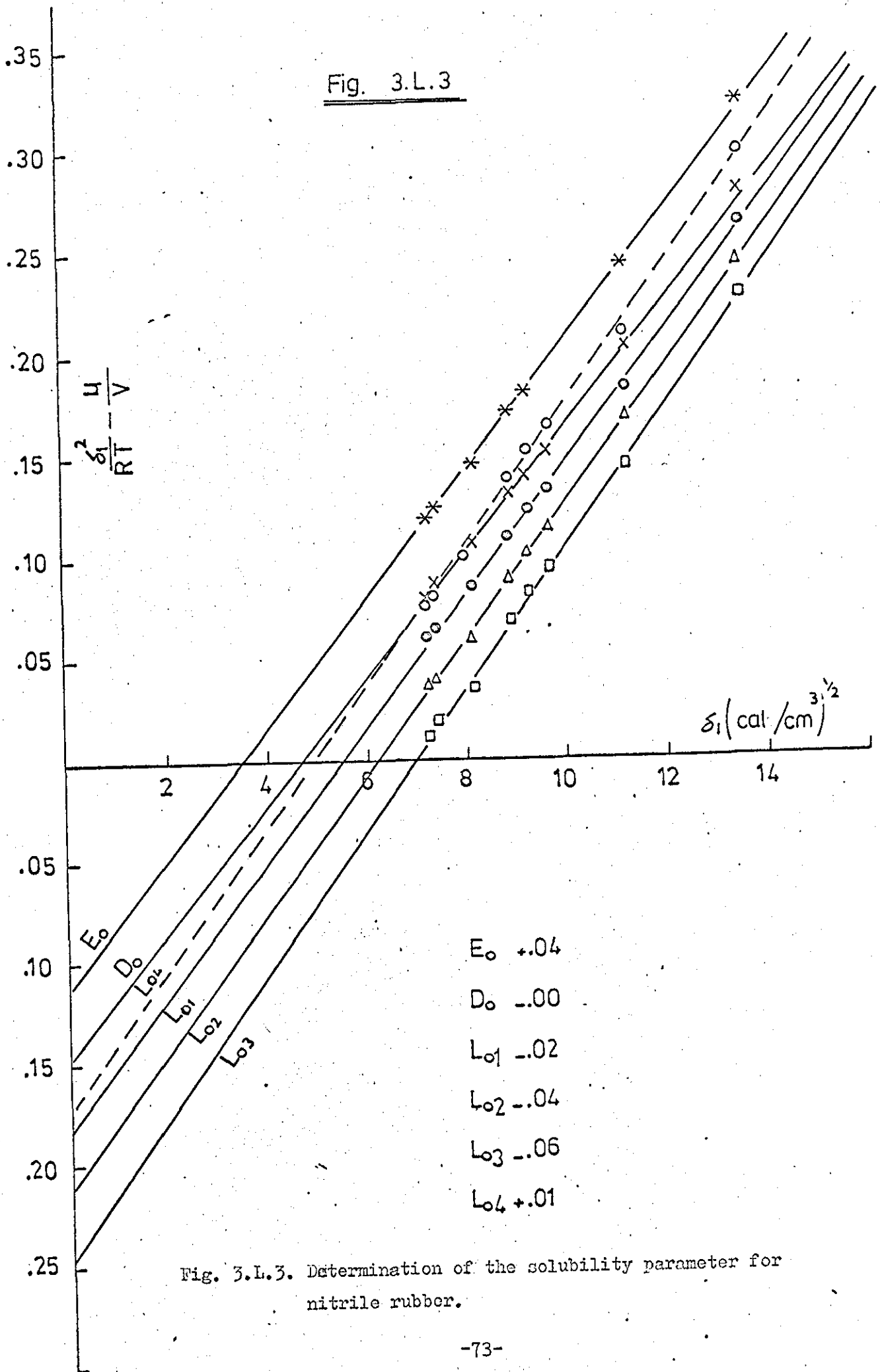
Fig. 3.L.3. Determination of the solubility parameter for nitrile rubber.
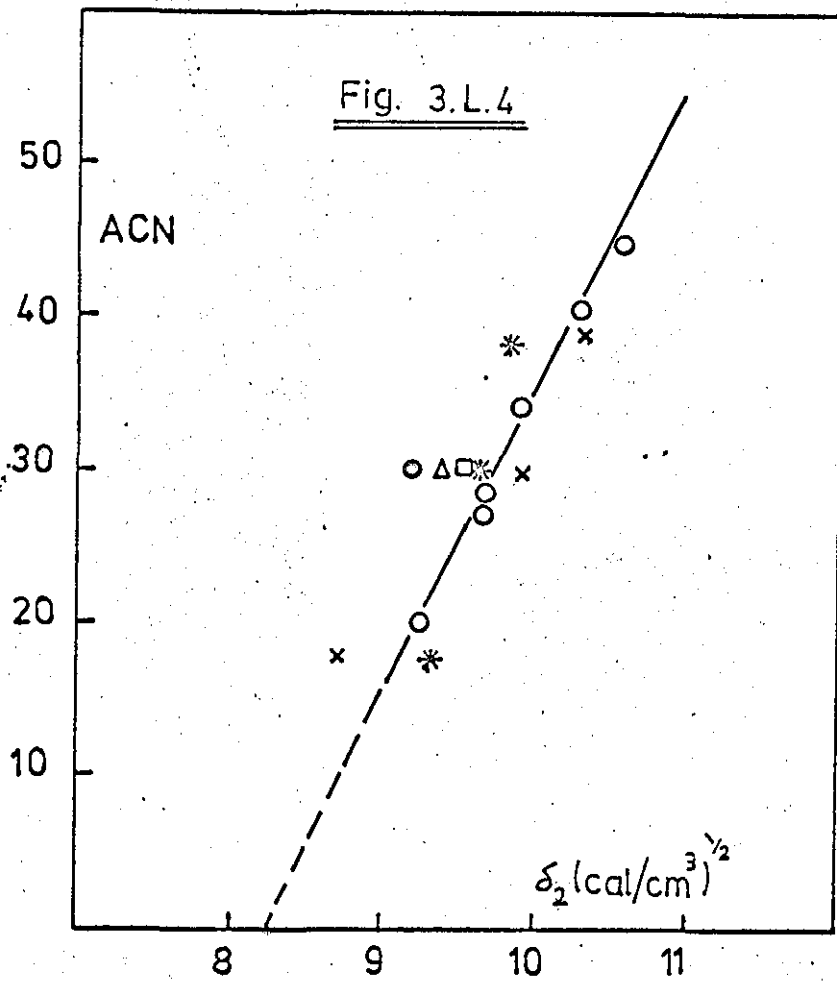
Fig. 3L.4 _ Relation between δ_2 and ACN, ○ Lawandy, ✕ Bristow
✳ Bisio, ▢ Scott, Λ Gee , ◉ Small

3.7 AHEM Standard Nitrile Mix - Mix E

In 1968 a report was been published by the Association of
Hydraulic Equipment Manufacturers (AHEM), proposing the
adoption of a seal compatibility index for mineral oils based
on the volume change of a standard rubber mix. A linear corre-
lation was established between the volume change of the
standard rubber and that of six commercial nitrile rubber mixes
in a range of 52 oils.

In 1970, Blow extended this work using 14 mixes of known
composition and five oils. Having established that the slope
of the line in the above mentioned plot of S.C.I.[*] v_s volume
change depended on the ACN content of the polymer, and its
position relative to the axes on compounding variations, the
suggestion was made, that compounders could characterise each
nitrile mix in terms of two constants representing these two
characteristics of the relationship.

In this section, the results of an investigation are
reported using the polymer and oils employed in the AHEM work.

The polymer used is Polysar Krynac 802. The solubility
parameter has been determined in the previous section 3.6. The
formulation of the AHEM standard mix differs in two respects
from that used in the majority of work discussed in this
thesis a) the black used as filler is FEF at 50 p.h.r. b) the
cure system is different (see Table 3.E.1.).

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[*] SCI is defined as the percentage volumetric swell of AHEM
standard nitrile rubber in the oil under specified conditions.

Table 3.E.1. Mix "E" formulation (parts by weight)

Polysar Krynac 802 (28.7 ACN)	100.00
Zinc oxide	3.00
Monsanto Flectol H	1.00
Stearic acid	0.50
FEF (Black)	50.00
MC Sulphur	1.50
TMTD	0.50
CBS	1.00
Physical properties	
Hardness	72
Tensile strength, Kgf/cm^2	195.6
Stress at 100% strain, Kgf/cm^2	53.5
Elongation at break %	250

Data of extractables and swelling in a range of l.b.l., acetone, toluene and chloroform, are given in Table 3.E.2.

The G value (calculated from stress strain measurements) and G' value (from swelling measurements) are given in Table 3.E.3.

Table 3.E.2. Percentage volume changes V_1 and Extractable content percentage by volume E_x

Acetone		Toluene		Chloroform	
ΔV_1	E_x	ΔV_1	E_x	ΔV_1	E_x
145.1	4.7	207	3.9	238.8	8.2

Table 3.E.3. Comparison data between stress-strain measurements
G and corresponding values G' obtained from swelling

G	Acetone $\mu = .543$		Toluene $\mu = .373$		Chloroform $\mu = .345$		Mean G'	G/G'
	v_r	G'	v_r	G'	v_r	G'		
1672	.4080	1465	.3261	1823	.2951	1636	1643	1.02

3.8 Interaction of polymers and oils

In this study, the interaction constant between the six
pure gum mixes used before and the seven oils $ASTM_1$, TELLUS 27,
50/50 $ASTM_{1,3}$, STOCK 27, DTD 585, $ASTM_3$ and STOCK 23 are investi-
gated.

Free swelling determinations $\Delta V_{(x)}$ of preextracted rectangular
samples in oils at $100°C$ have been carried out. The molecular
volume V of each oil was determined in accordance with the method
given in 2.7. From stress strain value G Table 3.L.6. equilibrium
swelling value v_r and molecular volume of oil V, the interaction
constant μ in equation (46) is calculated and given in Table 3.J.1.

Fig. 3.J.1. is a plot of μ v. v_r relating to six polymers
and seven oils, Fig. 3.J.2. is a plot of the volume swell of mix
Eo (the AHEM standard rubber in pure gum form, i.e. less the black)
v the volume swell of mixes Do, L_{01}, L_{02}, L_{03}, L_{04}, in the given
oils and Fig. 3.J.3. is the slope of the plots for each polymer
given in Fig. 3.J.2. v. the acrylonitrile content of the polymer.

(pure gum mixes)

Table 3.J.1. Interaction constants of polymers/and oil (μ) and the molecular volume of oils (MV)

Oil Name & molecular volume	E_o S.P. 9.63			D_o S.P. 9.20			L_{01} S.P. 9.64			L_{02} S.P. 9.88			L_{03} S.P. 10.3			L_{04} S.P. 10.57		
	ΔV_1	v_r	μ	ΔV_1	v_r	μ	ΔV_1	v_r	μ	ΔV_1	v_r	μ	ΔV_1	v_r	μ	ΔV_1	v_r	μ
ASTM$_1$ 649	5.6	.9470	2.144	10.4	.9058	1.797	6.6	.9381	2.003	2.9	.9718	2.671	0	1.000				
TELLUS 27 414.6	14.0	.8772	1.529	22.4	.8170	1.240	14.8	.8711	1.482	7.7	.9285	1.929	4.0	.9615	2.438	1.6	.9843	3.230
ASTM$_{1,3}$ 401.5	21.4	.8237	1.268	32.1	.7570	1.037	21.4	.8237	1.252	12.0	.8928	1.610	6.5	.9390	2.050	4.5	.9569	2.337
STOCK 27 376.5	24.8	0.8013	1.205	36.0	0.7353	1.006	21.9	.8203	1.259	12.6	.8881	1.595	6.7	.9372	2.039	5.0	.9524	2.266
DTD 585 331.7	30.1	.7686	1.116	43.6	05964	.931	27.0	.7814	1.158	17.1	.8540	1.414	9.7	.9116	1.780	7.7	.9285	1.944
ASTM$_3$ 384.1	43.8	.6955	0.938	60.6	.6627	.782	37.3	.7283	.994	21.8	.8210	1.270	14.8	.8711	1.500	10.1	.9083	1.751
STOCK 23 341.3	47.9	.6761	.915	68.0	.6761	.759	42.4	.7022	.952	25.4	.7974	1.199	16.0	.8621	1.463	13.0	.8850	1.593
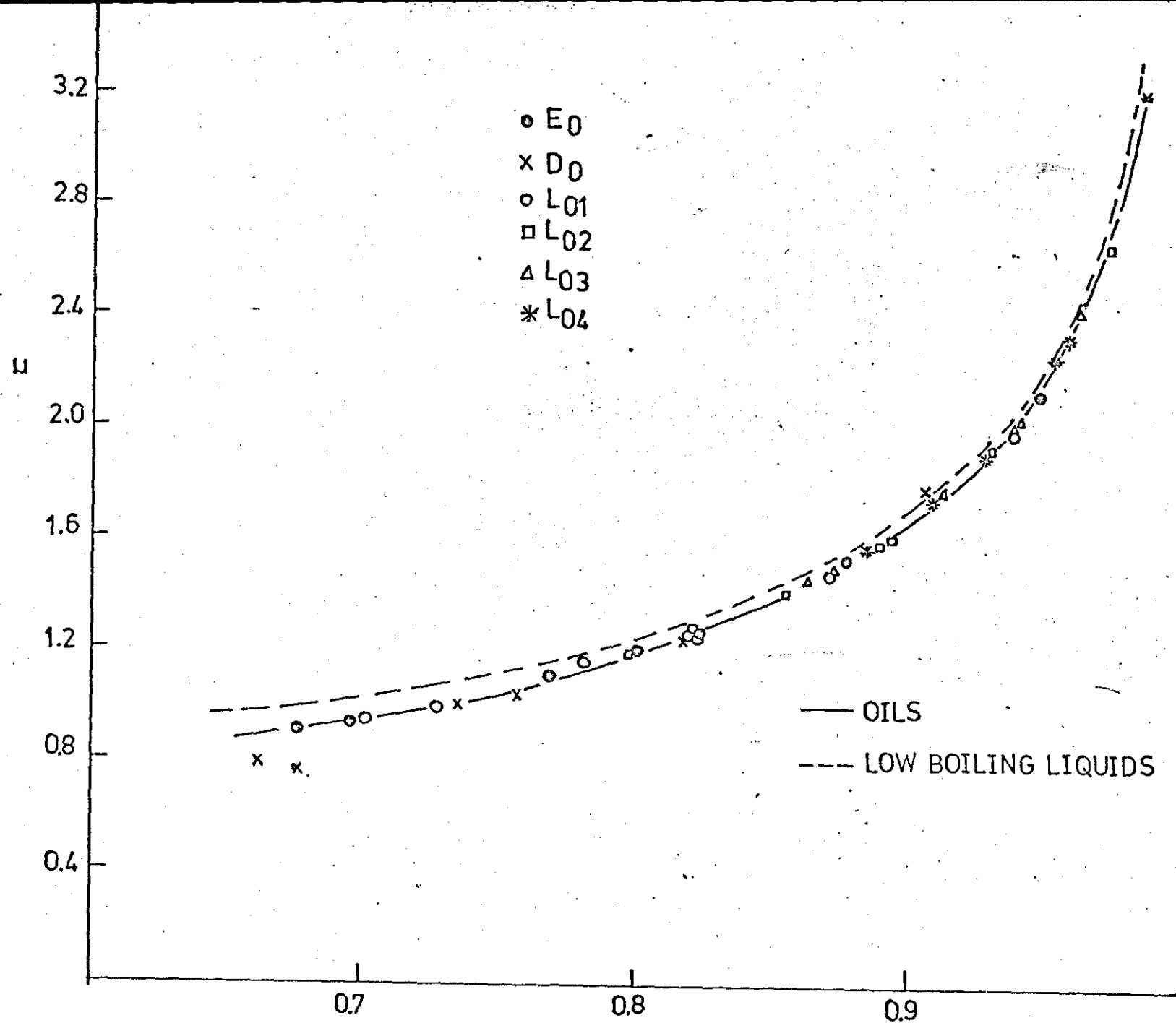
Fig. 3.J.1.   Relation between interaction constant μ and v_r (oils)
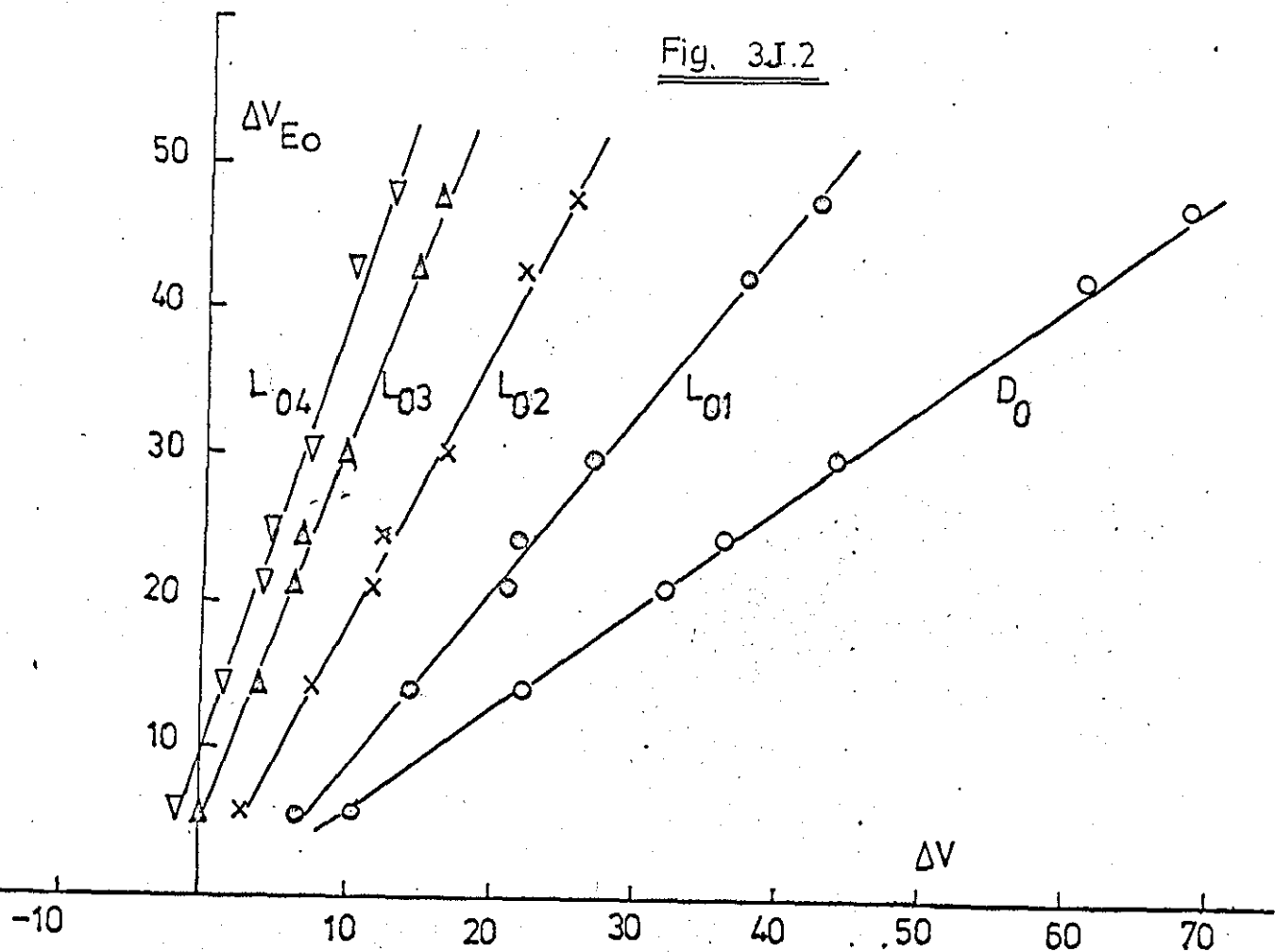
Fig. 3.J.2 _ Relation between volume swell of mix $E_o(\Delta V_{EO})$ and volume swell of the other five mixes.in oils .Pure gum mixes . Data from table 3.J.1.
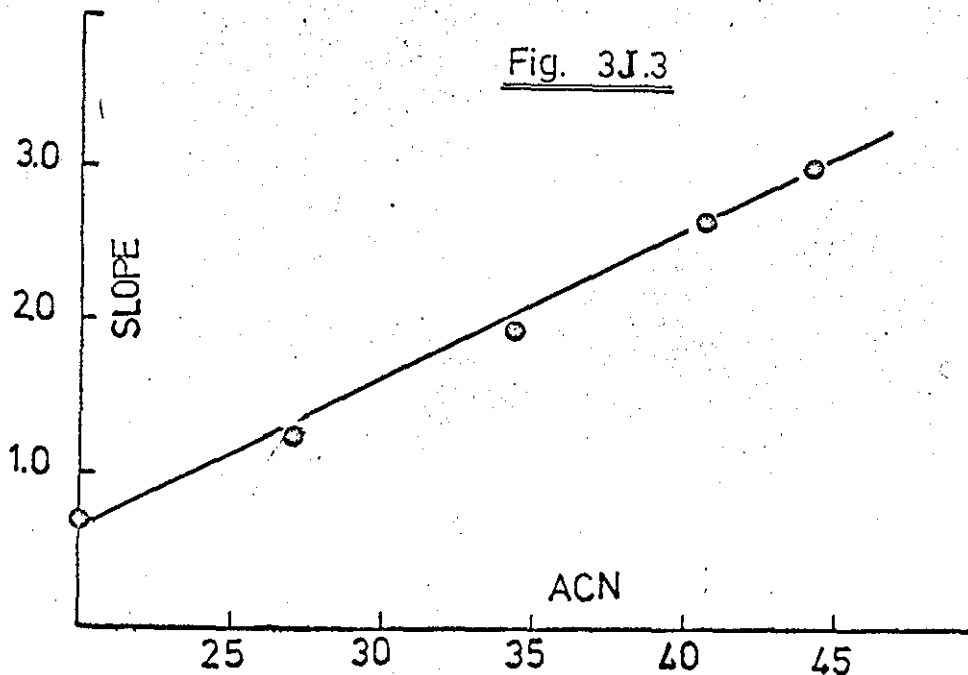
Fig. 3.J.3 _ Relation between the slopes of curves given in figure 3.J.2 and the ACN

Section 4

DISCUSSION OF FREE SWELLING RESULTS

The swelling behaviour of a nitrile rubber in a particular liquid depends greatly upon the acrylonitrile content of the polymer. In fact, it depends on the interaction constant between the polymer and the liquid, which in turn depends on the value of cohesive energy density of both the liquid and polymer; this will be examined more closely later.

The resistance of nitrile rubber vulcanisates to swelling can be increased by using a filler of small particle size, Table 3.A.4, or by increasing its amount; and varied by the choice of curing system Table 3.C.5. and by selecting a polymer of higher or lower nitrile content Table 3.L.5. By lengthening the cure time no remarkable effect on swelling has been noted (Table 3.D.1); that means that in the case of the mixes studied in this investigation, 20 min at $150^{\circ}C$ can be adopted as a cure time.

The theoretical relation between the volume fraction of rubber in the swollen gel v_r and G value from stress strain measurements is due to Flory and Rehner (equation 46). Fig. 3.A.3. and 3.B.2. show how, in the case of one polymer and different fillers, the G value versus v_r relationship varies from liquid to liquid. In liquids producing high swell (low v_r) v_r is more sensitive to G variation.

The swelling values ΔV of mixes containing thermal black loading can be equalised by a suitable correction:

$$\Delta V' = \frac{\Delta V \times V_m}{100} \qquad (66)$$

where ΔV is the percentage volume change of filled rubber (see Section 2.9.2) and V_m is the volume of mix containing 100 volumes of polymer. Table 4.K.1. shows the fair agreement between results

of pure gum mix and the corrected results of filled thermal black rubber using this equation.

Table 4.K.1. Comparison data between calculated and experimental swelling values for filled rubbers.

Mix No	%-PT	Acetone		Toluene		Chloroform		Stock 23	
		Uncorrected	Corrected	Uncorrected	Corrected	Uncorrected	Corrected	Uncorrected	Corrected
A_0	0	-	308	-	237	-	613	-	23.5
A_1	35	223	296	180	239	426	565	17.8	23.6
B_2	50	204	288	169	238	390	550	16.1	22.7
C_4	100	187	301	149	240	344	554	13.6	21.9

With small particle reinforcing blacks, no such equality is found. Kraus (1963) developed a theory for restricted swelling of reinforced filler rubbers in liquids. The theory relates the volume fraction of pure gum rubber in the swollen phase v_{ro} to the volume fraction of filled rubber v_{rf} and a constant parameter ϕ depending on the filler.

$$v_{ro}/v_{rf} = 1 - \left[3 \phi (1 - v_{ro}^{1/3}) + v_{ro} - 1 \right] x \; \frac{c}{1-c} \qquad (67)^*$$

To subject this theory to the experimental results obtained, the swelling values obtained by A_o-A_4 mixes in acetone, Table 3.A.3, were used to calculate the constant parameter ϕ. These values are given in Table 4.K.2. The obtained values for ϕ are about 50% more than those reported by Kraus using natural rubber, SBR and Butyl. Porter (1967) reported also the unexplained differences using natural rubber.

* Symbols used by Kraus have been changed to avoid confusion with characters in our earlier equations.

Table 4.K.2 Values of ϕ (Kraus equ. 67) from swelling in

Acetone - (Series A mixes)

Black type	FT	SRF	FEF	HAF
ϕ	1.363	1.690	1.830	1.657

Assuming that these constants are not affected by the solvent
used, a comparison can be made between the calculated and
experimental (using Kraus equation) swelling values for filled
rubbers, the experimental data being given in Section 3.2. This
is shown in Tables 4.K.3. and 4.K.4.

Table 4.K.3. Comparison of data between calculated and experi-
mental swelling values for filled rubber in toluene.

Mix No	A_1	A_2	A_3	A_4
Calculated	177	147	134	150
Experimentally	180	156	147	161
% error	-1.7	-5.0	-8.8	-6.8

Table 4.K.4. Comparison of data between calculated and experi-
mental swelling values for filled rubber in chloroform.

Mix No	A_1	A_2	A_3	A_4
Calculated	400	341	270	318
Experimentally	426	309	267	332
% ERROR	-6.1	+10.3	+1.1	-4.2

A similar study can be made with the B_2 mix (35 parts of SRF black p.h.r.) and B_3 mix (25 parts of HAF black p.h.r.) to show that the parameter ϕ is independent of the carbon black amount. This is shown in Table 4.K.5.

Table 4.K.5. Comparison of data between calculated and experimental swelling values for B_2 and B_3 mixes

Mix No	Liquid	Acetone	Toluene	Chloroform
B_2	Calculated	235	177	436
	Experimentally	223	181	403
	% ERROR	+5.4	-2.2	+8.2
B_3	Calculated	261	206	485
	Experimentally	241	193	441
	% ERROR	+7.6	+6.3	+9.0

From these results a general agreement of all types of black with the Kraus equation is shown and further the parameter ϕ is independent of the liquid and the amount of carbon black present within ± 10%. That means that in the case of butadiene acrylonitrile copolymer the presence of filler has no effect on the yield of crosslinks inserted by the crosslinking agent.

In the case of one oil (Stock 23) the relation between the equilibrium volume swelling ΔV and the penetration rate P for different acrylonitrile contents and different black types and amounts is of interest. Plotting this relation, Fig. 4.K.1, ~ p.91. a good straight line is obtained showing that P and ΔV are proportional. The equation behaviour can be represented by the equation:

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$$\Delta V = 90 \, P + 2 \qquad\qquad (68)$$

The intercept value may be explained by the extraction of ingredients by the oil.

The extraction of ingredients by liquid is one of the important factors in studying swelling behaviour. Blow (1972) has pointed out that the soluble ingredients of nitrile mixes are not fully extracted by mineral oils; there appears to be a relation between the amount of swelling and amount of soluble ingredients diffusing from the rubber into the oil. Fig. 4.K.2. shows a comparison of data given by Blow, relating to three different polymers with a set of five oils, with the data from Table 3.L.3. relating to four different polymers with one oil (Stock 23). There is a similarity in the two sets of results.

With a wider range of l.b.l. the trend is the same over a wide range of ΔV values (Table 4.K.6. and 4.K.7.).

Table 4.K.6. % volume changes and extractable content by volume for D_o and L_{04} mixes

Solvent	D_o Mix		L_{04} Mix	
	E_x	ΔV_1	E_x	ΔV_1
Chloroform	13.7	685	10.9	745
Toluene	12.0	421	7.4	143
Acetone	10.4	170	9.6	376
Cyclohexane	8.7	76.5	0.35	2.5
n-heptane	7.6	30.6	1.00	1.5

Table 4.K.7. % volume changes and extractable contents by volume n-heptane and toluene

Mix No	N-Heptane		Toluene	
	E_x	ΔV_1	E_x	ΔV_1
D_o	7.6	30.6	12.0	421
L_{01}	4.2	19.3	9.2	332
L_{02}	1.5	9.4	7.8	237
L_{03}	1.2	3.4	8.7	169
L_{04}	1.0	1.5	7.4	143

A plot of the values ΔV against E_x from Tables 4.K.6 ~~and~~ ~~4.K.7~~. show an interesting relation (Fig. 4.K.4.) in which the maximum extraction is higher than the total volume of soluble ingredients in the mixes indicating that, at higher volume swelling, a liquid such as chloroform attacks the rubber itself.

A relationship between ΔV and E_x for filled rubber mixes in Stock 23 oil and pure gum mixes in l.b.l. (n-heptane) can be shown in Fig. 4.K.3. From the graph it seems that the relationship is of the same nature.

The Flory-Huggins interaction constant, μ, has been obtained for the various nitrile rubber-liquid systems, from the equilibrium swelling and stress-strain data, Table 3.L.7. A plot of v_r against μ is shown in Fig. 3.L.2. From this graph, it is apparent that the expected error in calculating μ for liquids of very low swelling property is very high, and, therefore the G' values based on such μ values will be unreliable. This explains the choice of the three solvents - acetone, toluene and chloroform for this study. The same plot of v_r and μ (for polymer-oil) (Fig. 3.J.1.) has shown the same relation.

In this study the interaction constant is assumed to be unaffected by the variation of (i) the particle size and structure of carbon black (Series A) (ii) the polymer content (Series B) (iii) the cure system (Series C) and (iv) the cure time (Series D). The proof of this assumption has been attempted by calculating the ratio G/G' in all these cases. It has been found that this ratio is affected only by the carbon black type (Series A and B), but the cure time have been shown to cause no greater deviation than ± 0.05 in the value, (Table 4.K.8.).

Huggins deduced that the interaction constant μ is related to the square of difference between the solubility parameters of the liquid and the polymer - equation 49. The rearranged equation (50) enables the unknown δ_2 to be obtained from a series of μ and δ_1 values, including the possibility of recording low and high swelling liquids on the same plot, as shown in Fig. 3.L.3. Furthermore, using the intercept values, the μ_s value can be calculated and gives a value of 0.3, showing good agreement with the assumed value given by Scott and Magat (1949). Table 3.L.9. shows the agreement of results obtained for δ_2 from both slope and intercept (using $\mu_s = 0.3$) within a variation of ± 0.04.

Table 4.K.8 Condensed table – Comparison data between stres–strain measurements G and corresponding values G' from swelling

ACN	Filler		Cure* System	G	G'	G/G'
	type	amount				
20	FT	50	4	3111	2187	1.42
27.3	FT	100	4	2147	1558	1.38
34.4	FT	50	4	3269	2307	1.42
		65	4	2842	1997	1.42
		100	4	2395	1625	1.47
		100	1	3465	2364	1.46
		100	2	3685	2719	1.35
		100	3	2395	1625	1.42
	SRF	50	4	2207	1471	1.50
		35	4	3274	2247	1.46
	FEF	50	4	1663	1288	1.29
	HAF	50	4	2163	1694	1.28
		25	4	3369	2598	1.30
40.7	FT	100	4	2274	1549	1.47
44.1	FT	100	4	2319	1606	1.44

* As for C Series mixes Table 3.C.1.

The plot of the solubility parameter δ_2 against the acrylonitrile content is given in Fig. 3.L.4., together with the results obtained by Bristow and Watson (1958), Scott and Magat (1949), Sheehan and Bisio (1966), Gee (1943) and Small (1953). The solubility parameters are in closer agreement with those given by the first three authors than the results obtained by the last two authors. Sheehan and Bisio took an approach based on use of the parameter μ_s. They adopted a mean value $\mu_s = 0.34$ for all solvents, and they plot δ_1 vs $[RT(\mu - 0.34)/V]^{\frac{1}{2}}$ to derive δ_2. The measurements made by Gee and Small depend on the assumption that maximum swelling occurs when $\delta_1 \approx \delta_2$ and a plot of δ_1 against swelling will show a smooth curve with a maximum at $\delta_1 = \delta_2$. This method will in fact only give a general idea about δ_2.

As is to be expected the solubility parameter depends on the acrylonitrile content, and that relation has been shown to be linear (Fig. 3.L.4.) An extrapolation of this straight line to zero acrylonitrile content gives the solubility parameter of 8.25 for butadiene rubber in good agreement with values of 8.32-8.60 given in the literature (1966).

Consideration will now be given to the stress-strain measurements (of dry samples). A good linear relation passing through the origin is consistently obtained between the stress f/A_o and $\lambda - \lambda^{-2}$, where λ is the extension ratio indicating that the kinetic theory of elasticity is applicable to vulcanisates based on the butadiene acrylonitrile polymers, Fig. 3.A.2. and 3.B.1. Plotting f/A_o $(\lambda-\lambda^{-2})$ vs $1/\lambda$ to arrive at the C_1 and C_2 of the Mooney-Rivlin equation, on the other hand, shows that the slope is approximately zero, i.e. C_2 for nitrile rubber is equal to zero.

Therefore, the slope of f/A_o vs. $(\lambda - \lambda^{-2})$ plot has been used to calculate "G" from these stress-strain measurements and can be considered as depending on (i) the chemically crosslinked network introduced by vulcanisation (ii) the hydrodynamic effect of filler particles present in the rubber matrix (iii) attachments of rubber chains to the surface of filler particles (or polymer-filler interaction) and (iv) the entanglements of polymer chains.

Fig. 4.K.5. is a plot of G vs volume fraction of black C in the mixes. It is possible to interpret these as a linear relations which are fitted by the equations:

$$G = Go~(1 - 1.22~C) \qquad \text{For FT Black} \quad ....(70)$$

$$G = Go~(1 - 2.17~C) \qquad \text{For SRF Black} ....(71)$$

$$G = Go~(1 - 3.03~C) \qquad \text{For FEF Black} ....(72)$$

$$G = Go~(1 - 2.25~C) \qquad \text{For HAF Black} ....(73)$$

Where G and Go are the values for filled and pure gum mixes respectively.

The stress-strain curves of all rubber mixes depart from linearity and therefore the modulus has been taken as the slope of the best line through points up to 20% strain. A plot of the modulus,E,of filled rubbers and that, E_o, of pure gum Fig. 4.K.6. shows that the theoretical relationships proposed by Smallwood (equation 51) and Guth and Gold (equation 52) are not applicable to the nitrile rubber compounds studied. Up to a volume concentration of thermal black of 0.35,equation 53, due to Guth, however, shows a fair agreement with the experimental results, using a shape factor f_s equal to one.

A good agreement with this equation is also obtained for FEF black (up to C = 0.3) using a shape factor equal to 3. On the other hand this equation does not fit in the case of HAF and SRF black.
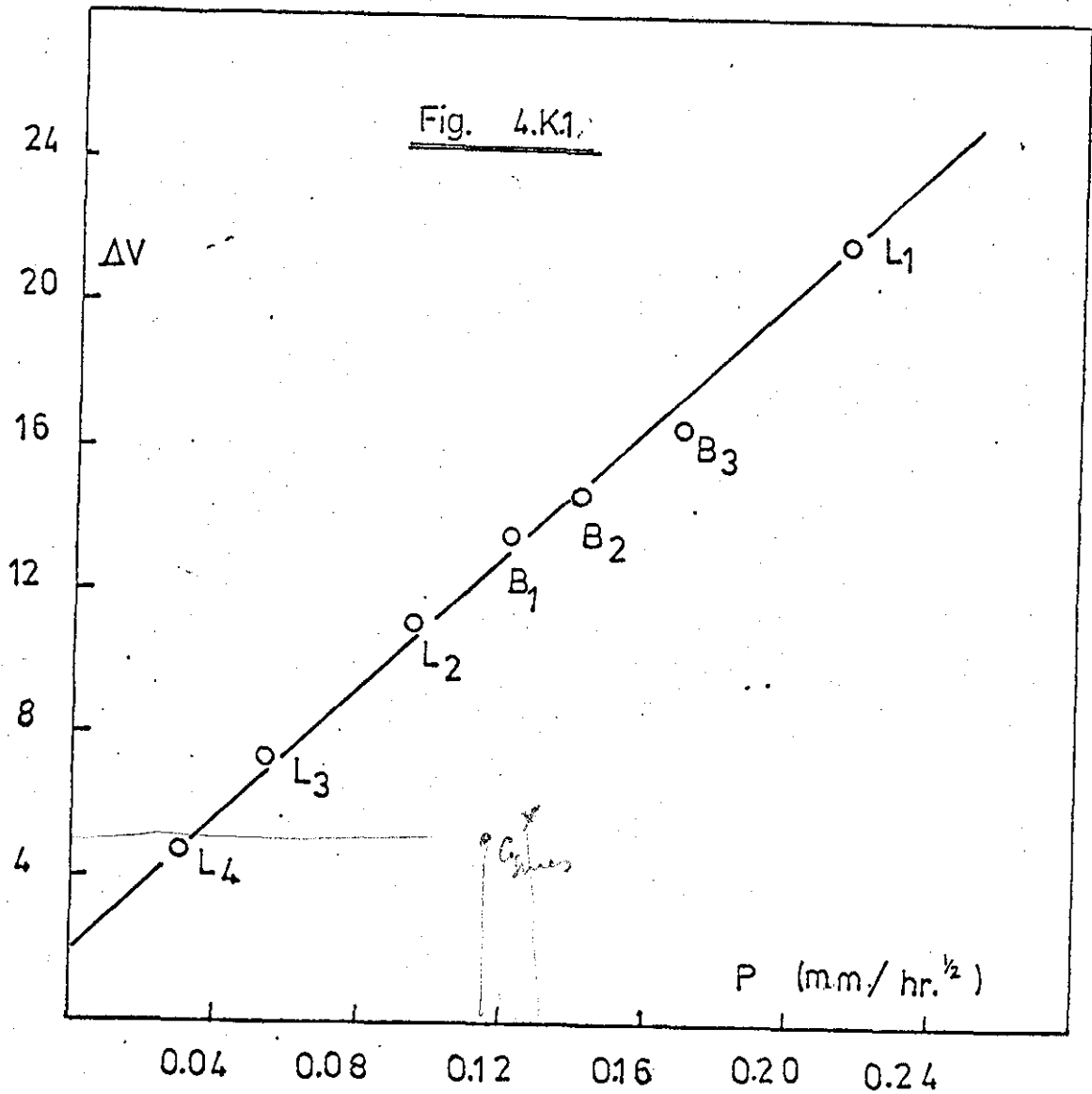
Fig. 4.K.1.

Fig. 4.K. 1. Relation between volume swelling "ΔV" and penetration rate "P." Stock 23 oil at 100°C

Fig. 4.K.2

ΔV_x

$$\frac{\Delta V_x - \Delta V}{E_x} = \frac{E_x'}{E_x}$$
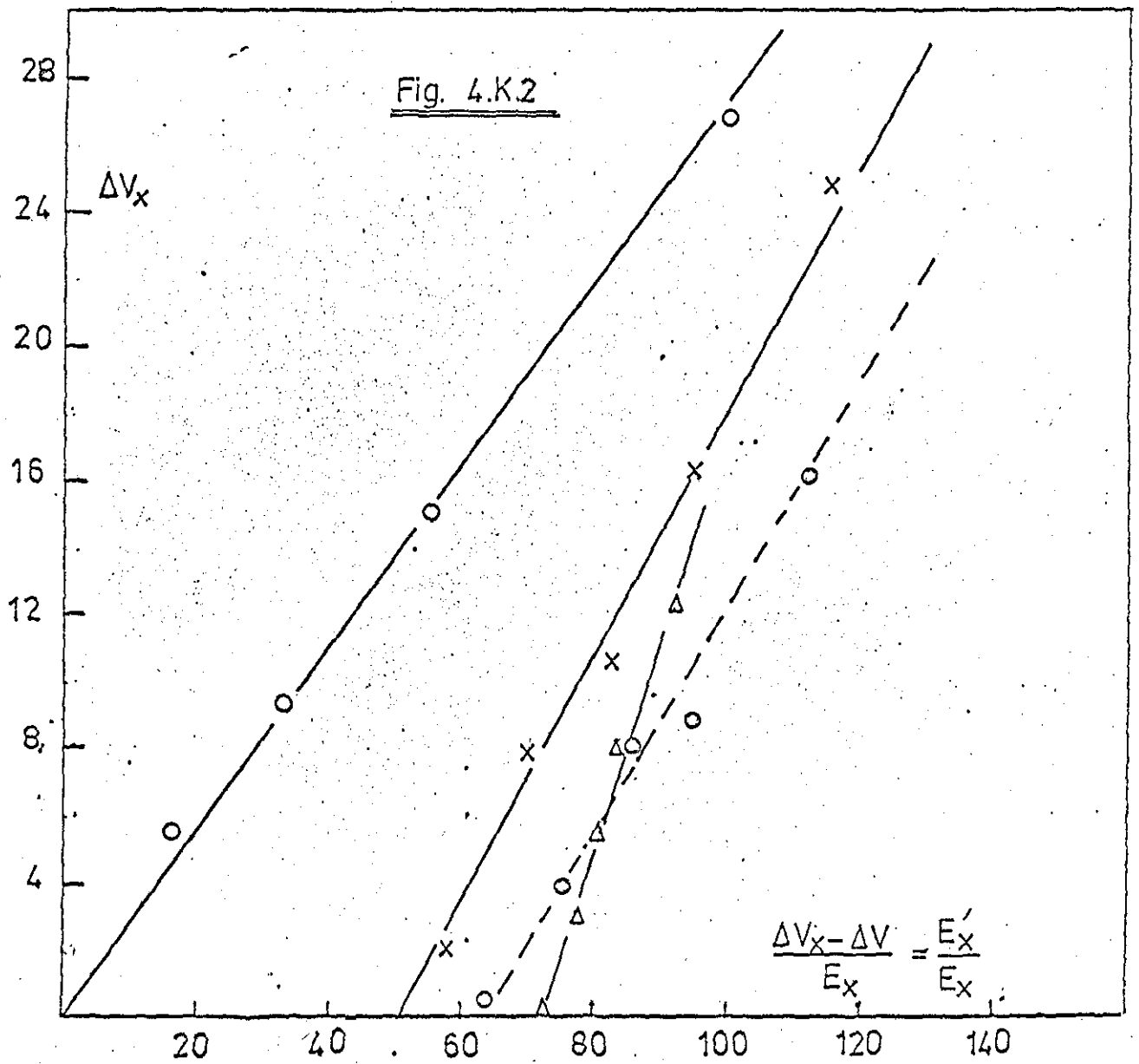
Fig. 4.K.2 Comparison data ; O Lawandy; × Δ O Blow.

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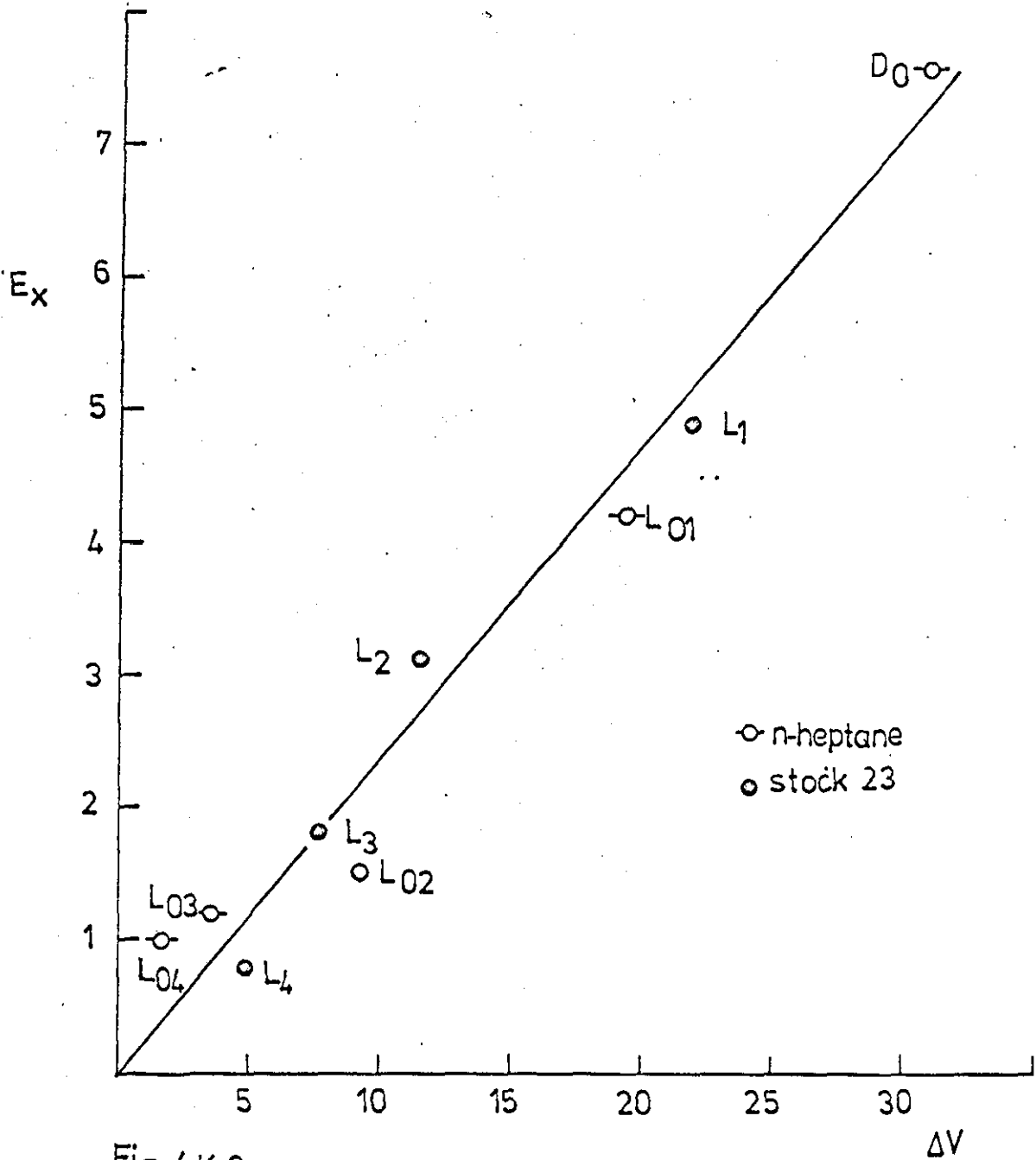
Fig. 4.K.3 ΔV against E_x for pure gum mixes in n-heptane and filled rubber mixes in Stock 23 oil .
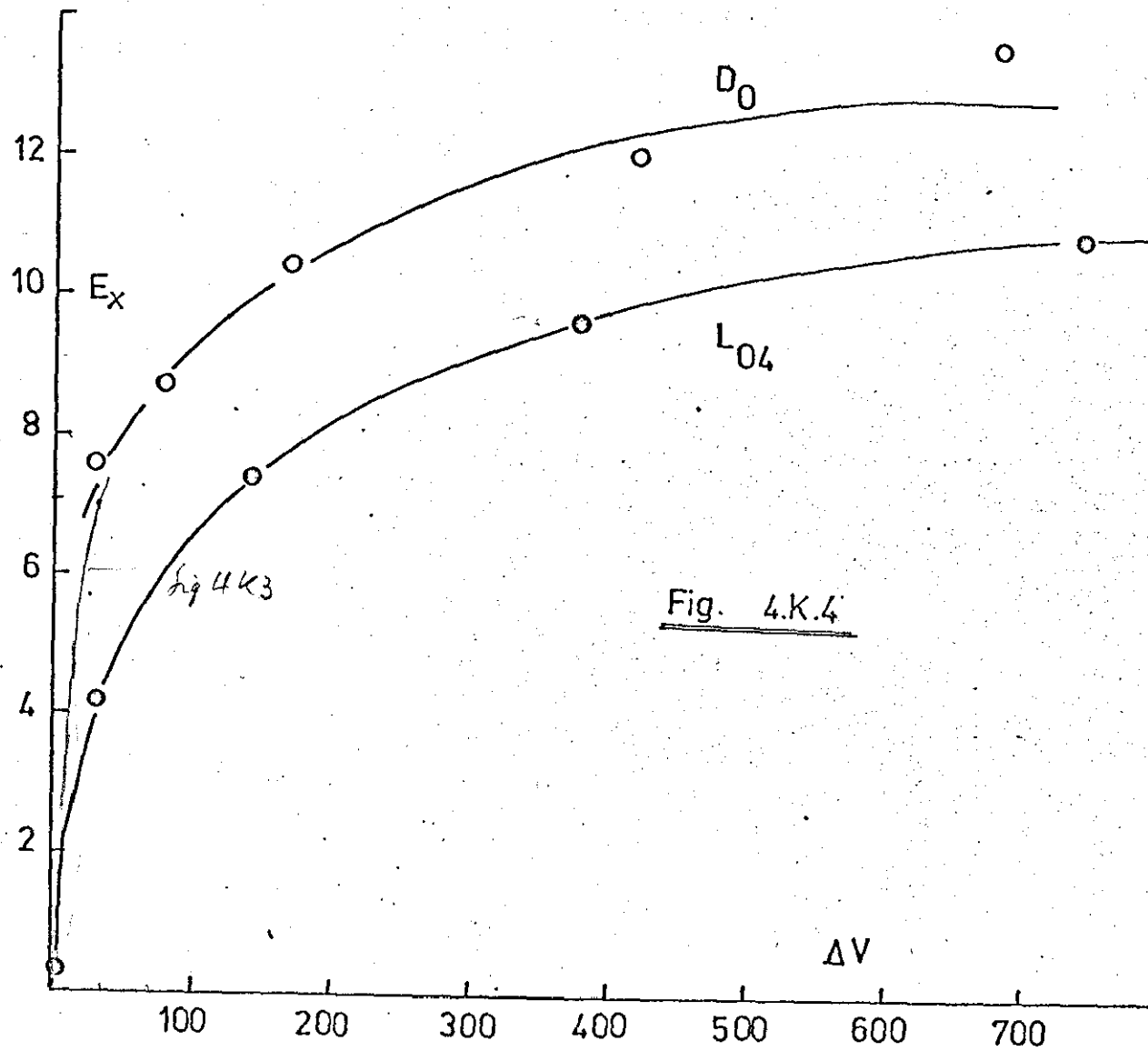
Fig. 4.K.4. Relation between volume swell (ΔV) and extraction (E_x).
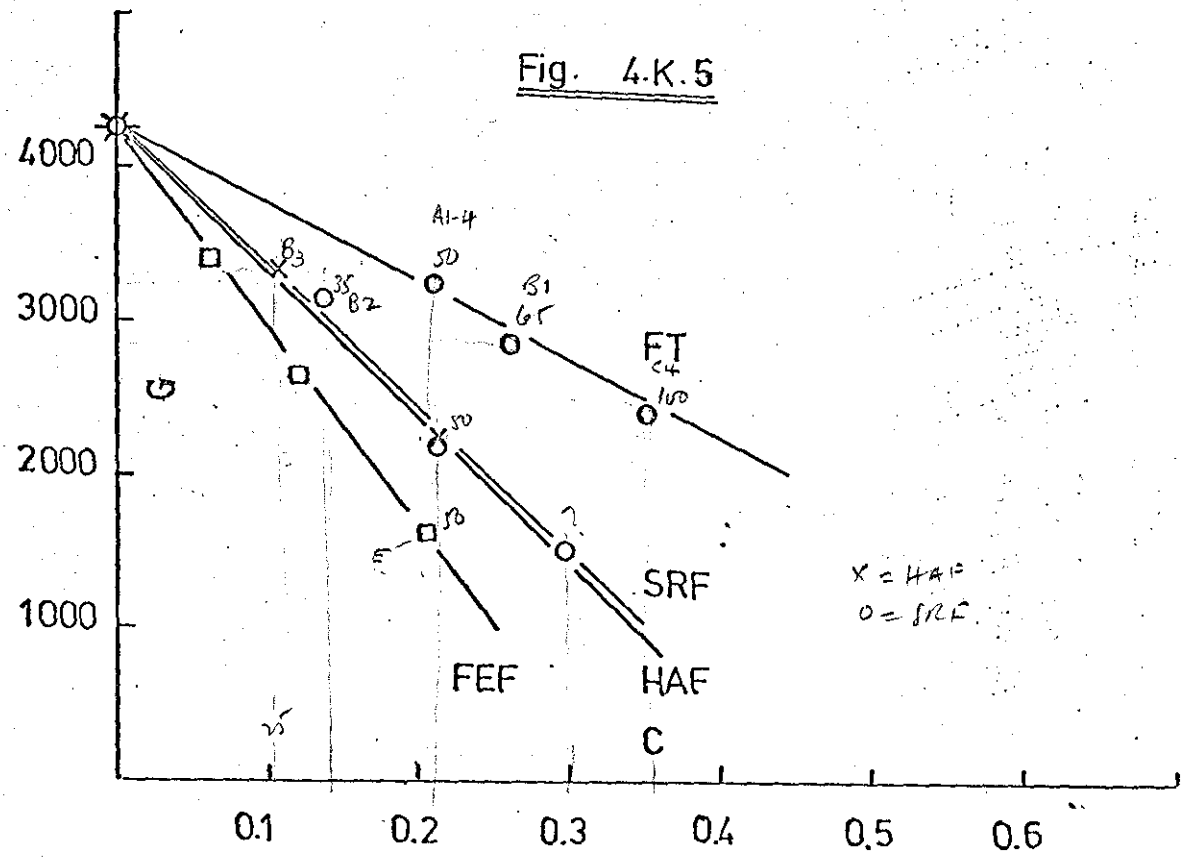
Fig. 4.K.5

Fig. 4.K.5.   Relation between (G) and volume fraction of black (C).
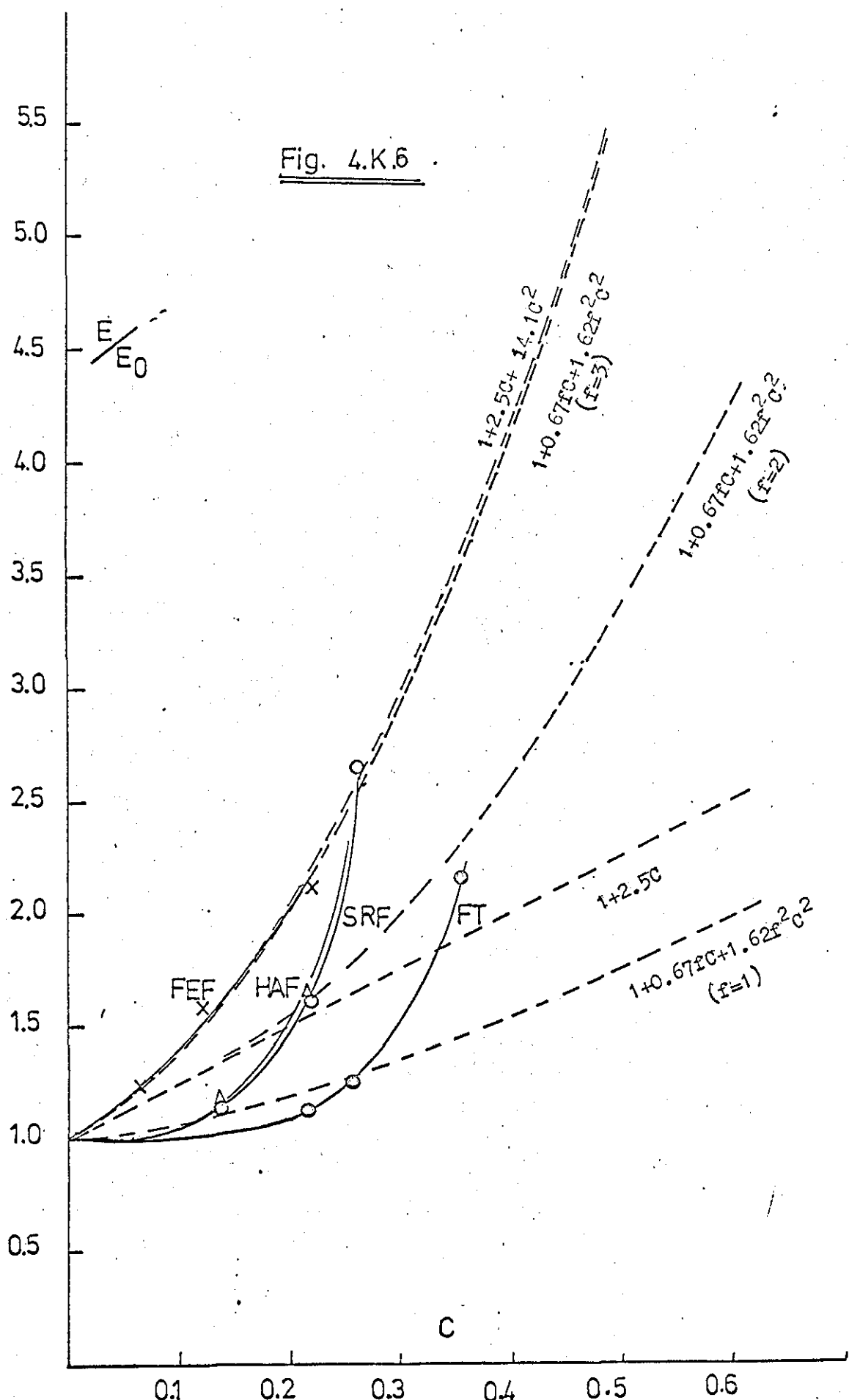
Fig. 4.K.6. Relation between E/E_0 and carbon black concentration (C)

SECTION 5

Swelling Under Compressive Strain

5.1 Effect of black type - Series A mixes

The four mixes A_{1-4} which contain carbon black of different particle size and structure have been used to study the effect of compressive strain on the percentage set and the equilibrium volume swelling. Cylindrical samples were used with Clamp (1), the curing time was 20 min at $150^\circ C$ and the oil used was Stock 27. The relation between the percentage set (CS) calculated by equation (63) and the time in days at compressive strains of 10, 15, 25 and 40% are given in Figures 5.A 1, 2, 3 and 4 . It is to be noted from this study that the percentage set increases with time and decreases with the increase of compressive strains; the maximum state of set is reached after 8 days.

The equilibrium swelling ΔV_s of these mixes at different strains are also calculated, Table 5.A.1. The relation between ΔV_s and $(100 - \% \text{ compression})^{\frac{1}{2}}$ is shown in Fig. 5.A.5.

The set values, at the point in time where the volume swell has reached the maximum, have been corrected for the degree of linear swell by the use of equation (65). The CS_c (referred to as the swelling-corrected set) are plotted against the percentage compressive strain. (Fig. 5.A.6.)

5.2 Effect of polymer content - Series B mixes

The mixes B_{1-3}, which contain different amounts and types of black to vary the polymer content and maintain hardness to be nearly constant, have been used to carry out the same study as for the A series. Cylindrical samples were used with clamp (1), the cure time was 20 min at $150^\circ C$ and the oil used was stock 27.

The relation between the percentage set and time in days at different compressive strains is given in Fig. 5.B. 1,2,3, 4. The curves show that the percentage set increases with time until about 8 days and then decreases as the sample tends to reach equilibrium swelling. It is also to be noted that the higher the polymer content the higher is the set.

The equilibrium volume swelling of these mixes at different compressive strains are calculated, Table 5.B.1., and the relation between ΔV_s and $(100 - \%\ \text{compression})^{\frac{1}{2}}$ is given in Fig. 5.B.5. Fig. 5.B.6. shows the relation between CS_e and the percentage compressive strain.

5.3 Effect of cure system - Series C mixes

In this series, the effects of the cure system on the percentage set and swelling under compressive strain have been investigated. Cylindrical samples were used with clamp (1), the curing time was 20 min at $150^\circ C$ and the oil used is Stock 27.

It is to be noted here that mix C_4 has the same cure system as mixes A_1 and B_1 and the same type of filler, FT black, the proportions being 100, 50 and 65 respectively. Fig. 5.C.1, 2, 3, and 4 show the relation of the percentage set against time for C_4, A_1 and B_1, from which it seems that, at the low compressive strains of 10-15%, the amount of carbon black has no effect on the set, but higher values of set occur with the higher amount of carbon black at 25 and 40 percent compression. Fig. 5.C.5, 6, 7, and 8 show the dependence of the set on the cure system, at different strains.

The equilibrium volume swelling of these samples are given in Table 5.C.1 . and the relation between ΔV_s and $(100 - \%\ \text{compression})^{\frac{1}{2}}$ can be shown in Fig. 5.C.9. Fig. 5.C.10 shows the relation between corrected set CS_e and percentage compressive strain.

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5.4 Effect of acrylonitrile content - Series L mixes

The four filled rubbers L_1 - L_4 of different acrylonitrile contents at a cure time 20 min at $150^{\circ}C$, (cylindrical samples used with clamp (1)) have been used to study the relation between square root of time and uptake of $ASTM_3$ oil at different compressive strains. Fig. 5.L.1. shows the linearity of the swelling with square root of time, through the origin.

Figs. 5.L. 2,3,4 and 5 are the plots of percentage set against the time in days for different compression. From the graphs it can be noticed that, (i) the percentage set increases with the increase of ACN . (ii) in the case of the two lowest ACN contents L_1, L_2 the percentage set decreases with time, whereas at the higher ACN L_3 and L_4 the percentage set increases with time, but in both cases there is a slight increase in the set after 8 days.

The equilibrium volume swelling of this series is given in Table 5.L.1 and Fig. 5.L.7. shows the linear relation between ΔV_s and $(100 - \% \text{ compression})^{\frac{1}{2}}$. Fig. 5.L.6. show the relation between the corrected set CS_c and the percentage compressive strain.

A dry compressive strain has been also carried out under the same condition for swelling compressive strain. Table 5.L.3. and Figure 5.L.8. are comparison data for dryset and corrected set CS_c.

5.5 The effect of test piece size on swelling under compressive strain

Mix D has been used to study the effect of test piece size on the percentage set and the equilibrium volume swelling. O rings M and L were used with clamp 2. The curing time was

20 min at 150°C and the oil used was Stock 27. The percentage set
CS and the percentage swelling at compressive strains of 10, 15
and 25% are given in Table 5.D.1. The relation between ΔV_s and
$(100 - \% \text{ compression})^{\frac{1}{2}}$ is shown in Fig. 5.D.1. and the corrected
set CSe against % compression is shown in Fig. 5.D.2.

5.6 Discussion

5.6.1. Swelling under compressive strain:-

The simple relationship between swelling values ΔV_s and the
square root of (100 - % compression) given by Blow et al (1969) and
derived from the expression given by Flory and Rehner (1944) has
shown good agreement with nitrile rubber in both low and high
swelling values, Figs. 5.A.5., 5.B.5., 5.C.9. and 5.L.7.

In plotting ΔV_s vs $(100 - \% \text{ compression})^{\frac{1}{2}}$ the acrylonitrile
content has shown different slopes (Fig. 5.L.7.). The slope of
these curves can be used to identify the A.C.N. and Fig. 5.L.9.
shows the plot of ACN   vs the slope of these curves.

In plotting the square root of time vs uptake of $ASTM_3$ oil,
at different compressive strain (Fig. 5.L.1.), the M_e/M_t values
at a certain time (t = 10 hr) obtained are 1.60, 1.64, 1.65 and
1.63.

Assuming that "S" the cross section area given in equation
(4) is constant, it can be concluded that, although the equili-
brium volume swelling is affected by different compressive strain
the penetration rate of a liquid into rubber is not changed.

5.6.2. The percentage compression set:-

Diffusion of liquid into rubber is known to change the
compression set. In investigating the different cases it was
found that the compression set of a test piece swollen to

equilibrium strain increases with (i) the increase of carbon black particle size and amount (ii) the increase of ACN in the particular formulation.

During the course of initial absorption of liquid by the test piece, the observed compression set changes linearly with time (Fig. 5.L.2-5), but the slope of these lines vary considerably. These slopes are plotted in Fig. 5.L.10 against ACN content for various compressive strain values. In Fig. 5.L.11. the same slope values are plotted against percentage compressive strain for the various ACN content.

A negative slope means that the absorption of liquid is predominant and more than counteracts the set increases. Positive slopes occur where the liquid absorption is low. As the compressive strain is increased swelling is decreased, resulting in a general change from negative to positive slopes.

Table 5.A.1. ΔV_s values at different compressive strain - cylindrical samples in oil stock 27 at $100^{\circ}C$

Mix No	10% comp	15% comp	25% comp	40% comp
A_1	4.1	3.3	3.2	3.2
A_2	3.8	3.9	3.6	3.2
A_3	3.8	3.8	3.6	3.2
A_4	3.9	3.9	3.5	3.6

Table 5.B.1. ΔV_s values at different compressive strain - cylindrical samples in oil stock 27 at $100^{\circ}C$

Mix No	10% comp	15% comp	25% comp	40% comp
B_1	3.7	3.5	3.4	3.1
B_2	4.5	4.3	4.0	3.9
B_3	4.5	4.5	4.5	4.1

Table 5.C.1. ΔV_s values at different compressive strain - cylindrical samples in oil stock 27 at $100^{\circ}C$

Mix No	10% comp	15% comp	25% comp	40% comp
C_1	3.3	3.0	2.4	2.1
C_2	4.0	4.0	3.7	3.3
C_3	3.2	3.0	3.2	3.0
C_4	3.2	3.2	2.8	2.6

Table 5.L.1. ΔV_s values at different compressive strain -
cylindrical samples in ASTM$_3$ oil at 100°C

Mix No	10% comp	15% comp	25% comp	40% comp
L_1	15.3	15.3	14.5	13.7
L_2	6.4	5.5	5.5	5.5
L_3	2.5	2.3	2.0	2.5
L_4	1.7	2.1	1.7	2.0

Table 5.L.2. Comparison data, dry set and corrected
set values (ASTM$_3$ oil) - cylindrical samples
carried out at 100°C

		10% comp	15% comp	25% comp	40% comp
	Dry set	52.5	48.5	45.3	52.3
L_1	corrected set	46.2	42.6	42.2	41.0
	Dry set	54.3	47.5	49.7	51
L_2	corrected set	58.8	48.2	51.4	51.7
	Dry set	62.9	60	65.0	66.7
L_4	corrected set	75.5	62.5	66.4	66.6

Table 5.D.1.   % CS on ΔV_s values at different compressive strain

for M and L O-ring samples in oil stock 23 at 100°C

	% Set CS			ΔV_s		
	10%	15%	25%	10%	15%	25%
O ring - M	64	34.1	13.8	41.7	41.3	39.1
O ring - L	69.4	38.9	10.6	41.7	41.0	38.4
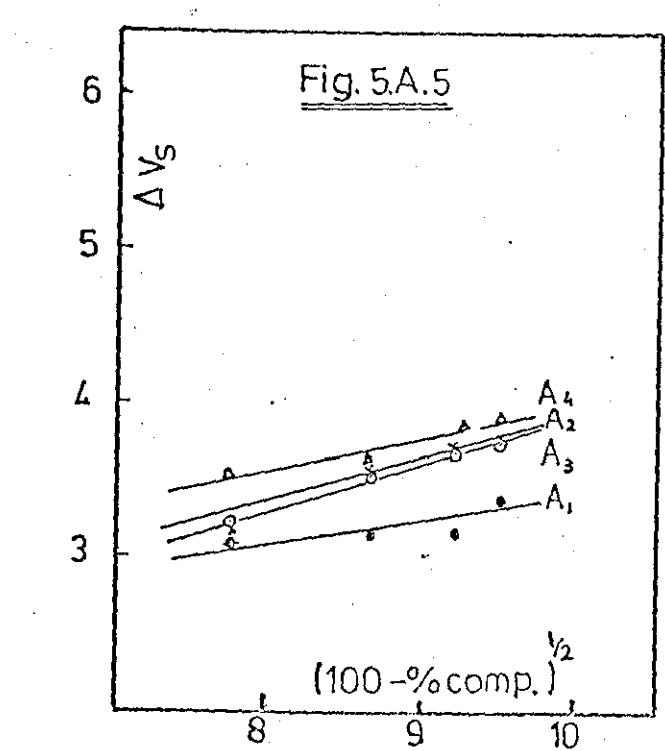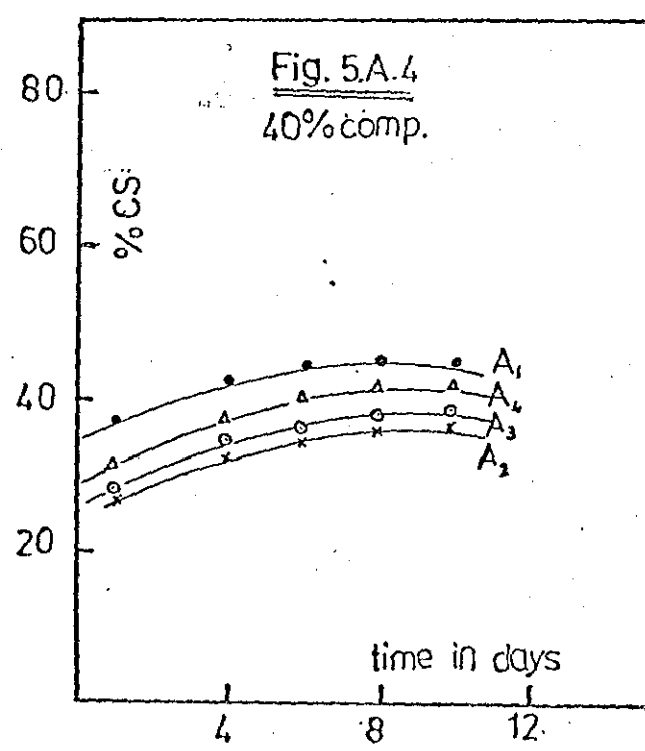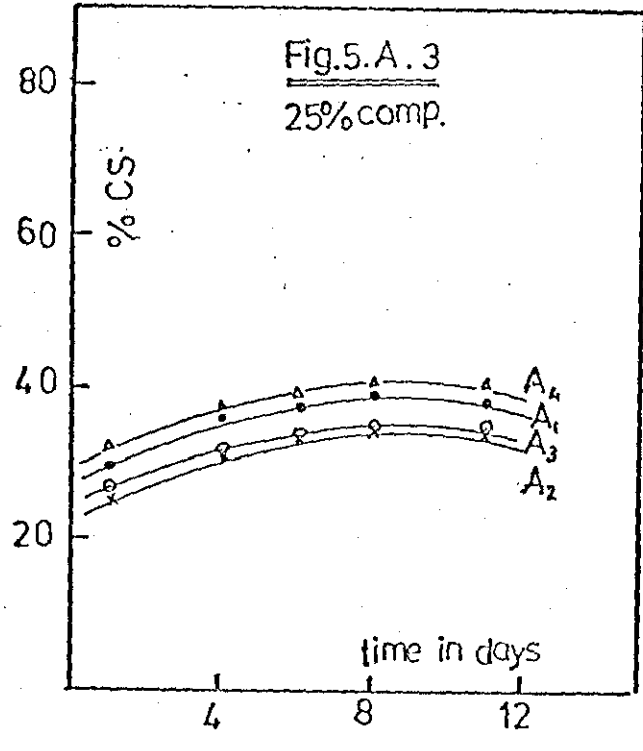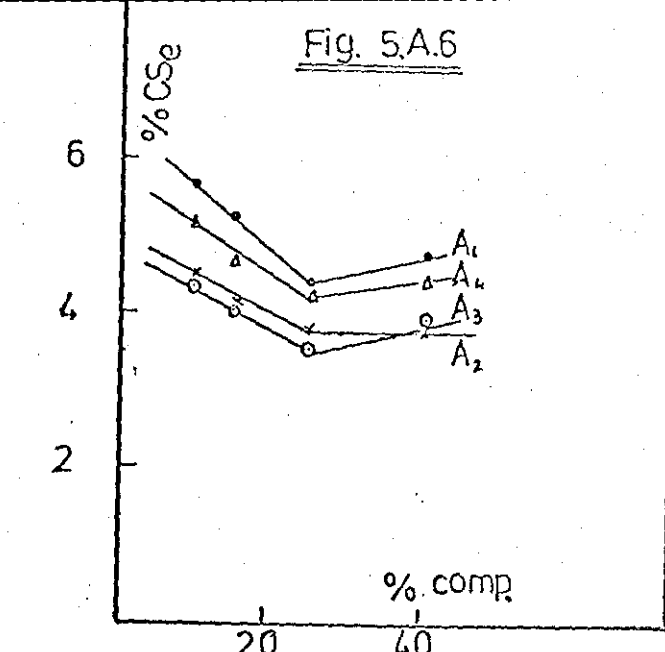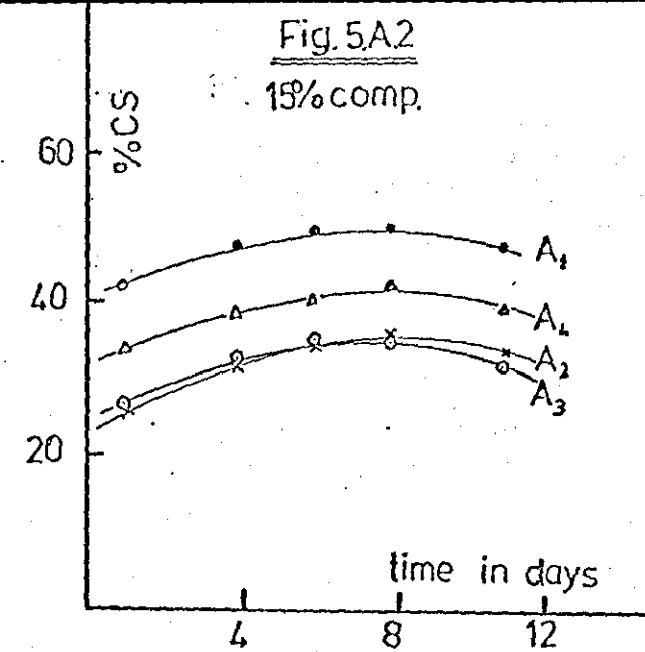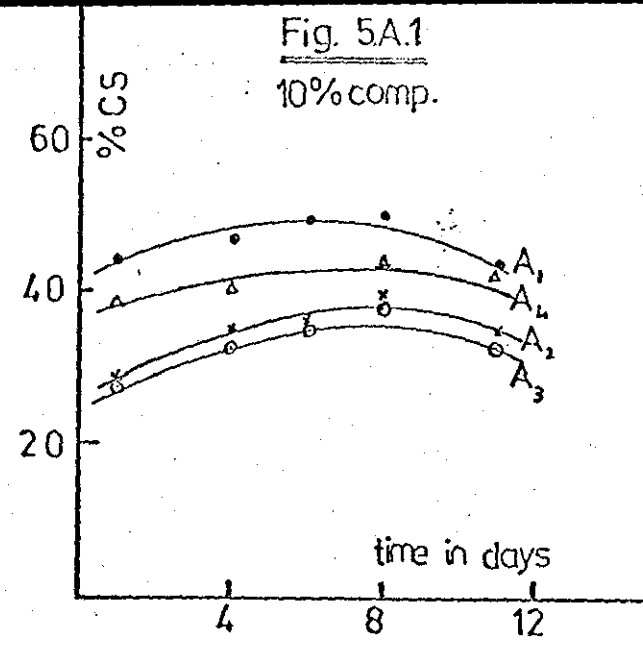
Swelling under compressive strain Series "A" mix.

Fig. 5.B.1 10% comp.

Fig. 5.B.2 15% comp.

Fig. 5.B.6

Fig. 5.B.3 25% comp.

Fig. 5.B.4 40% comp.

Fig. 5.B.5

Swelling under compressive strain Series "B" mix.

Fig. 5.C.1 — 10% comp.

Fig. 5.C.2 — 15% comp.

Fig. 5.C.3 — 25% comp.

Fig. 5.C.4 — 40% comp.

100 phr.
65 "
50 "
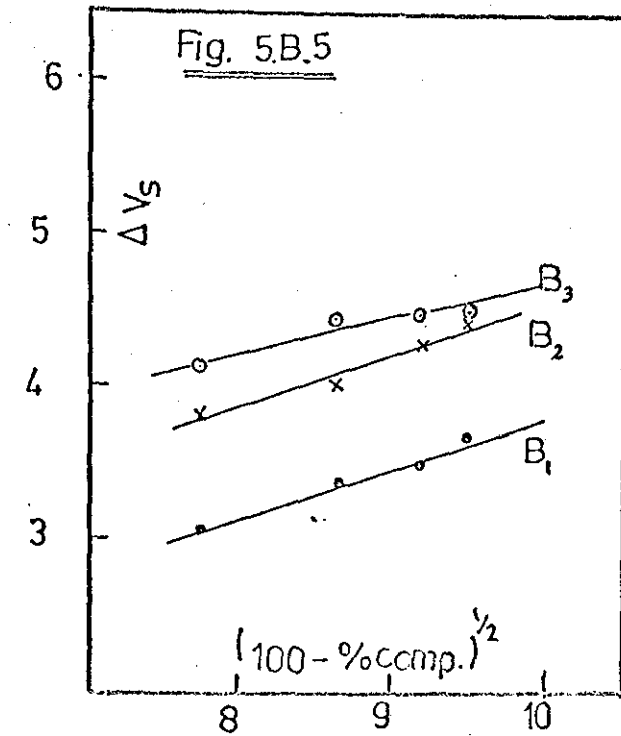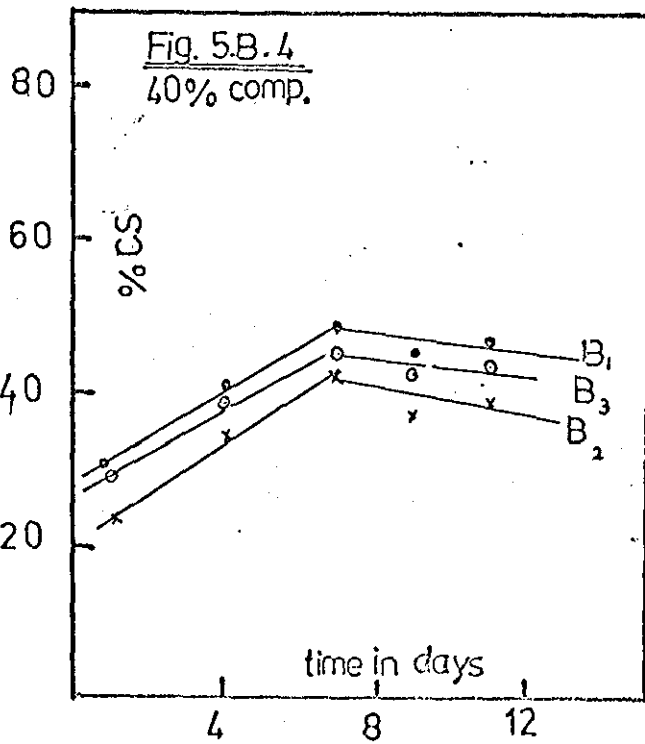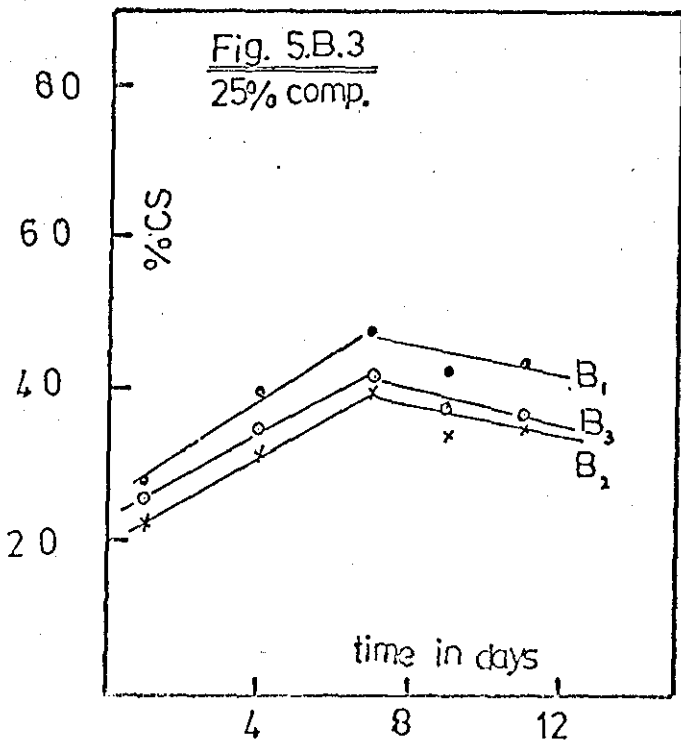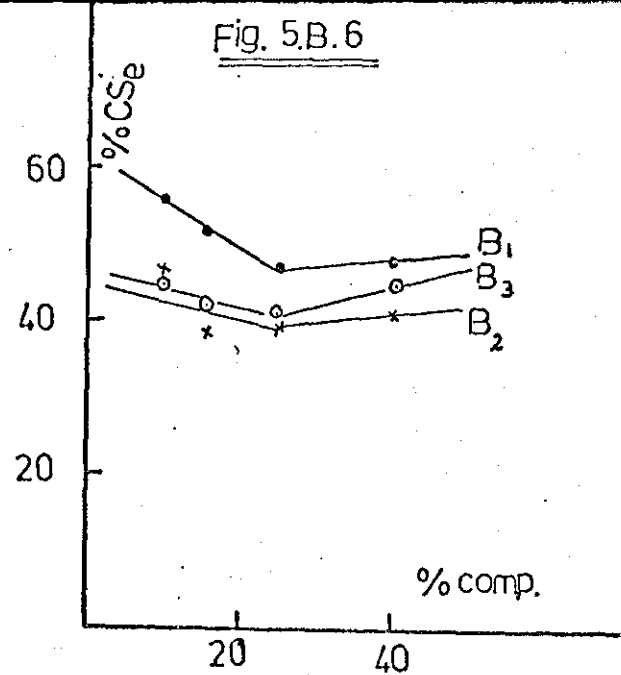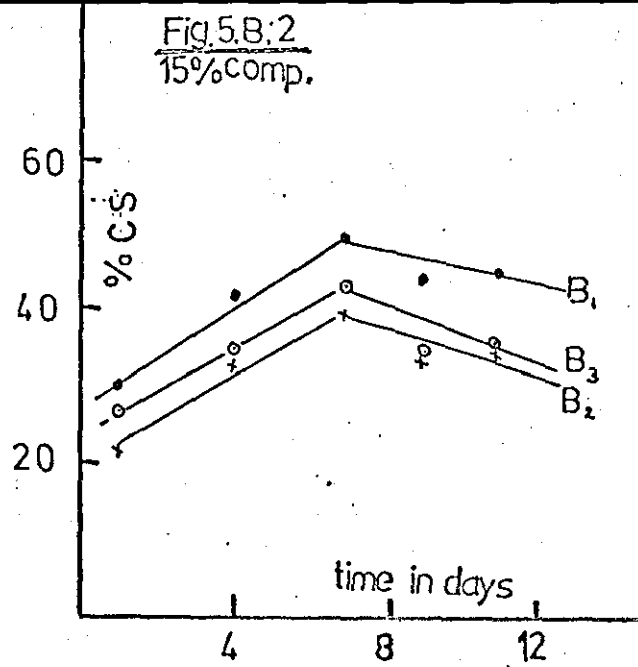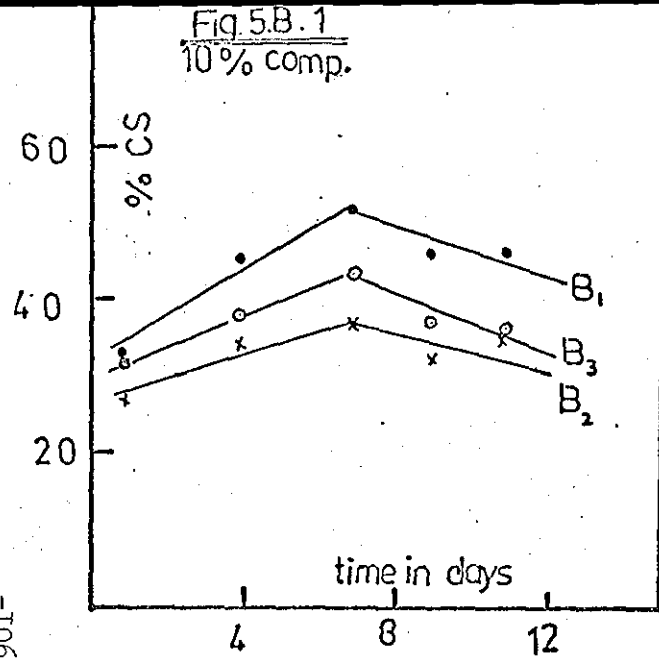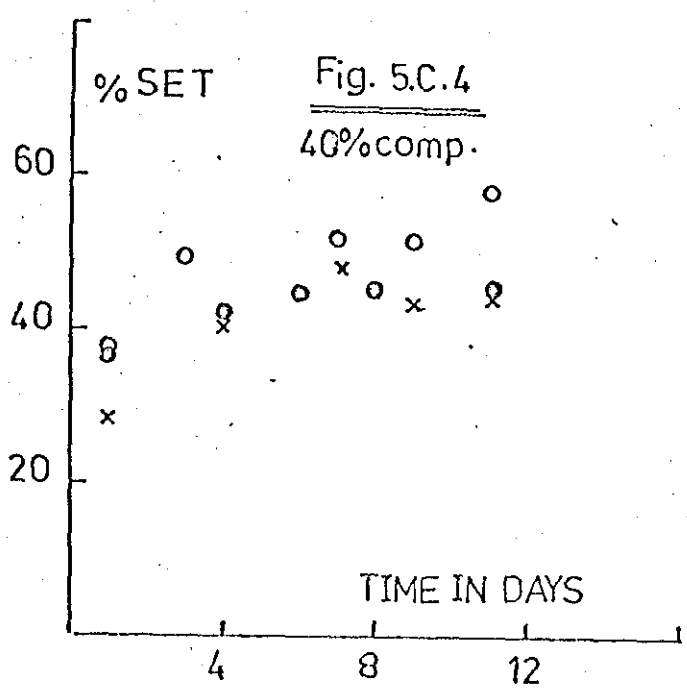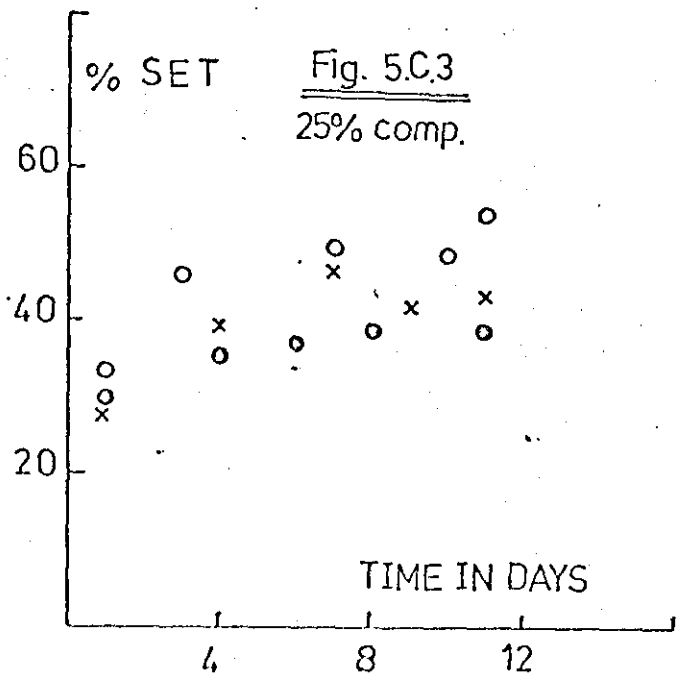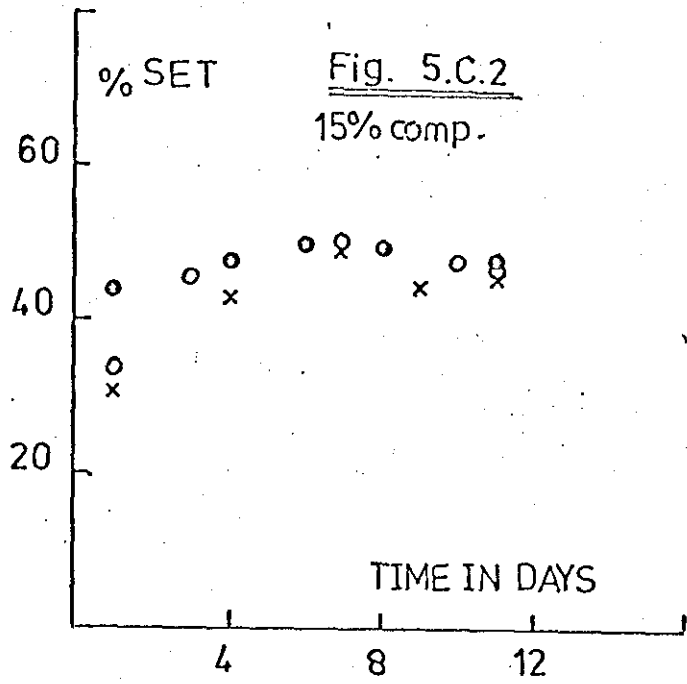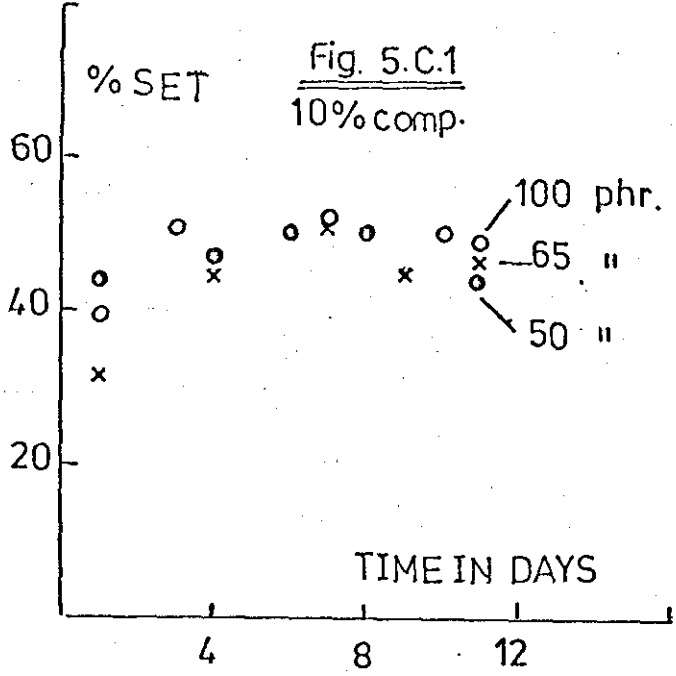
Effect of carbon black concentration on % compression set.

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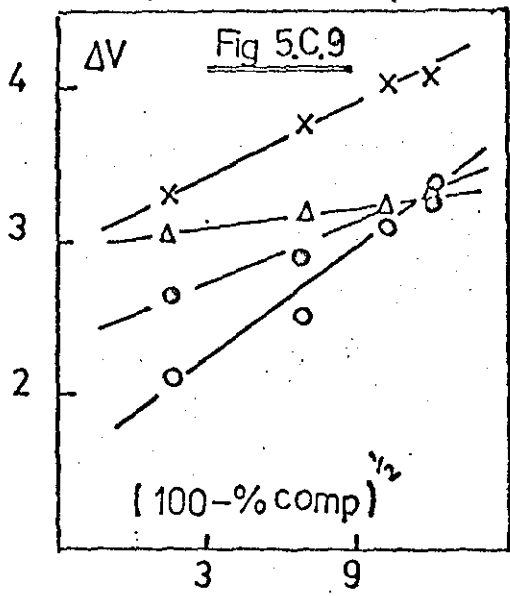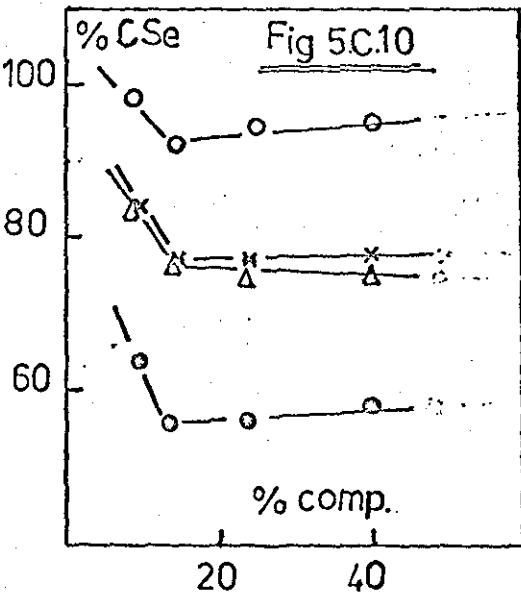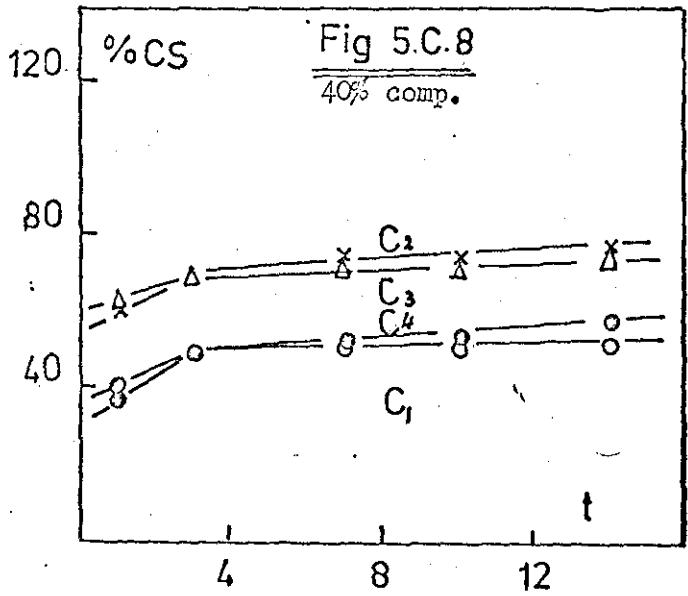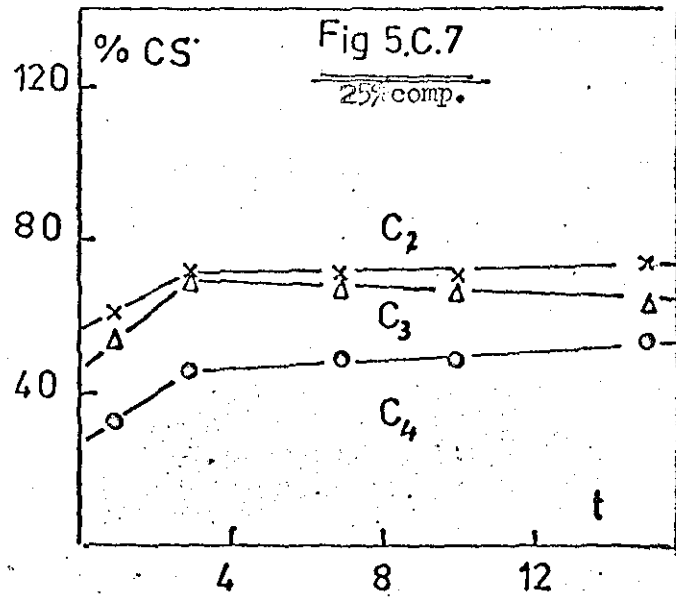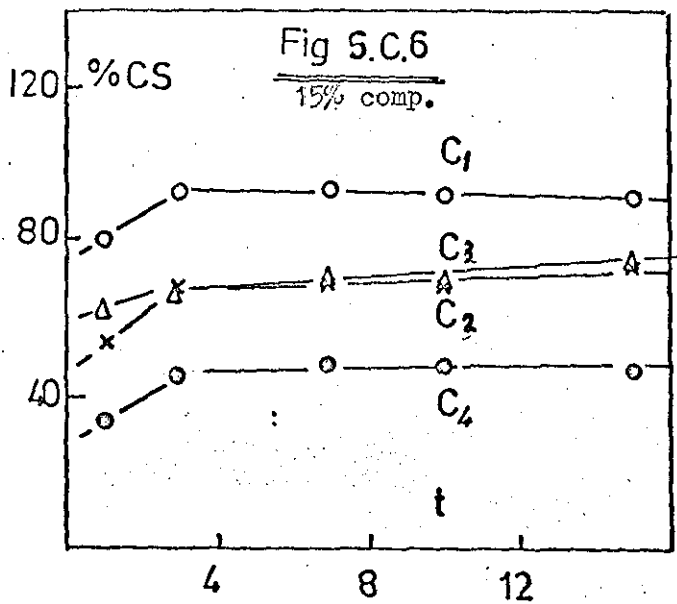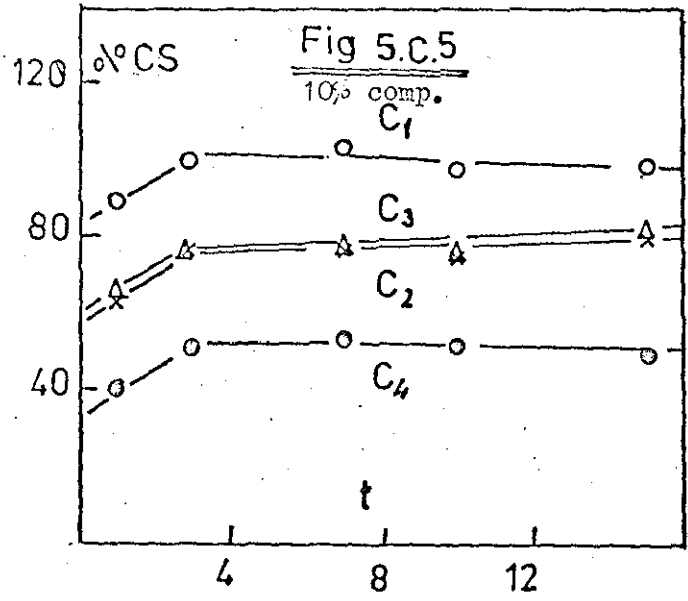
Swelling under compressive strain Series "C" mix.
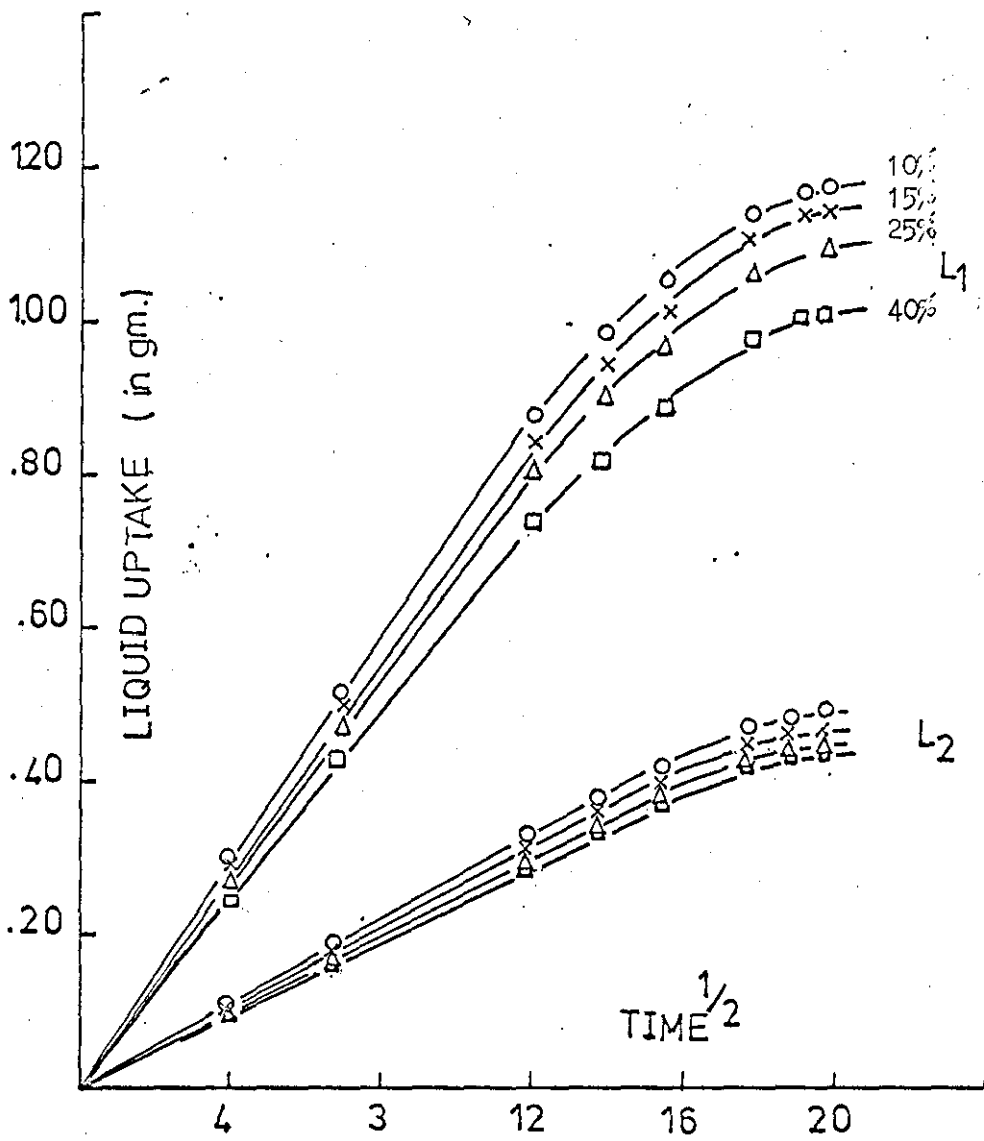
Fig. 5.L.1. Swelling curves under compressive strain.
10,15,25 and 40% compression.

Fig. 5.L.2 — 10% comp.
Fig. 5.L.3 — 15% comp.
Fig. 5.L.6
Fig. 5.L.4 — 25% comp.
Fig. 5.L.5 — 40% comp.
Fig. 5.L.7
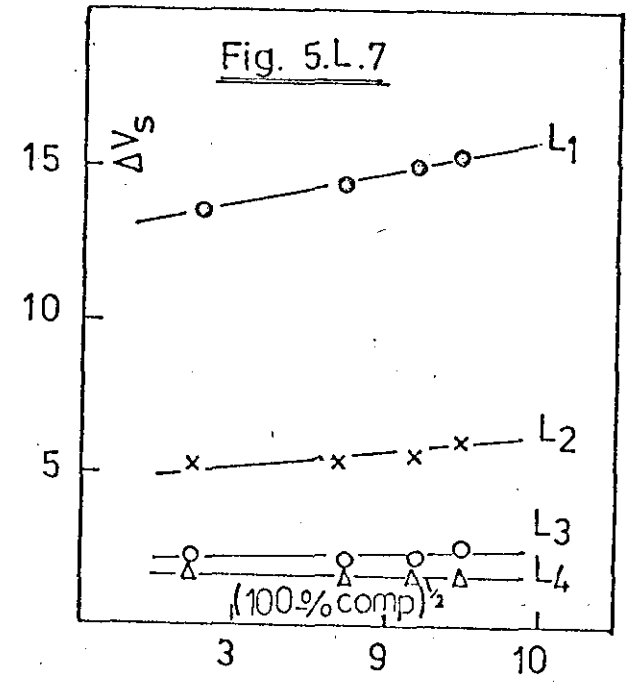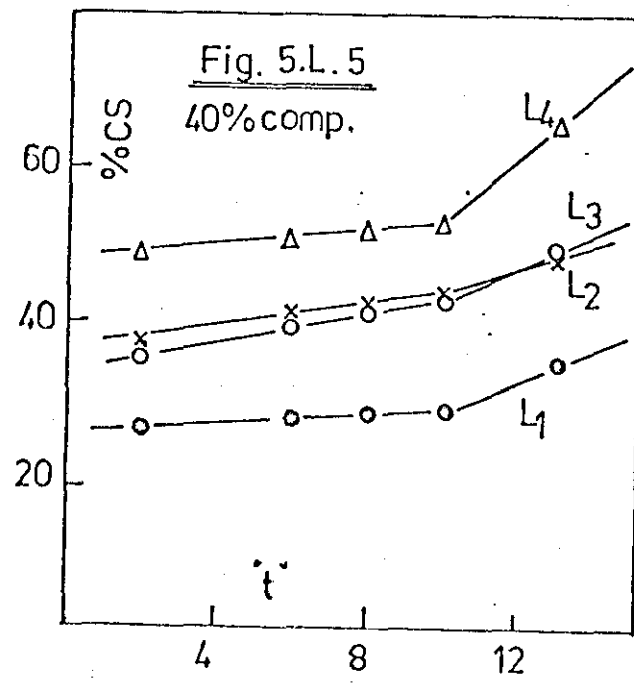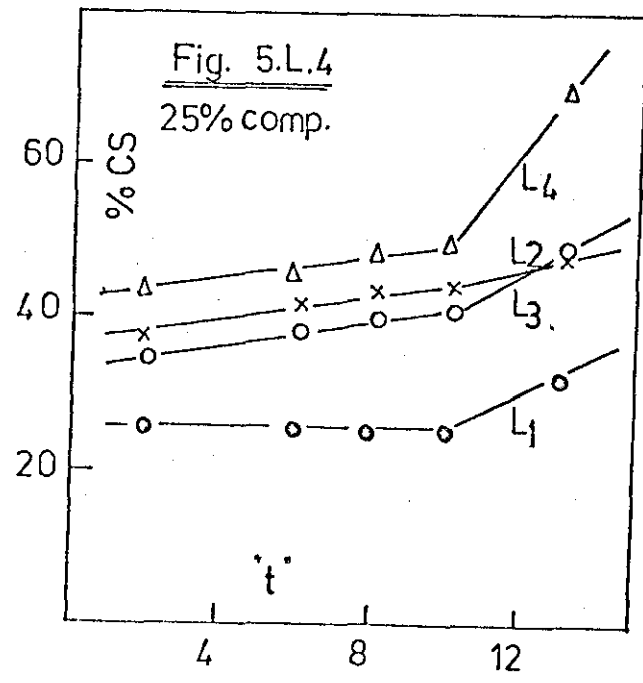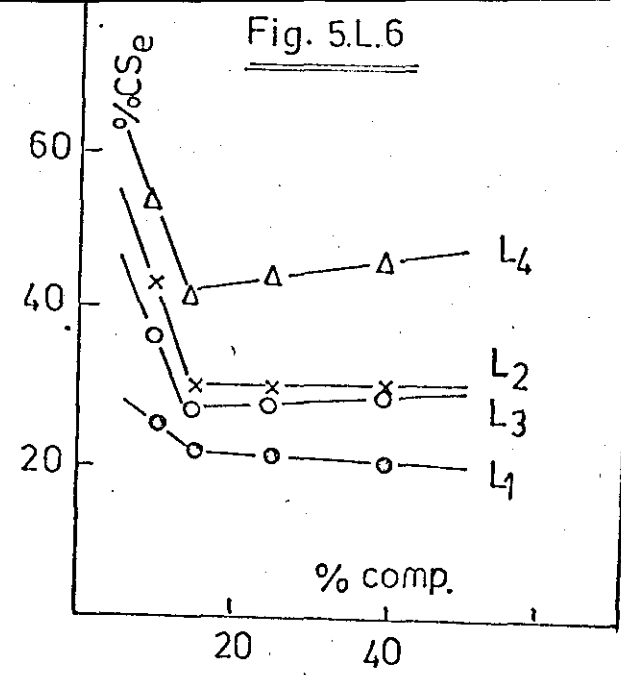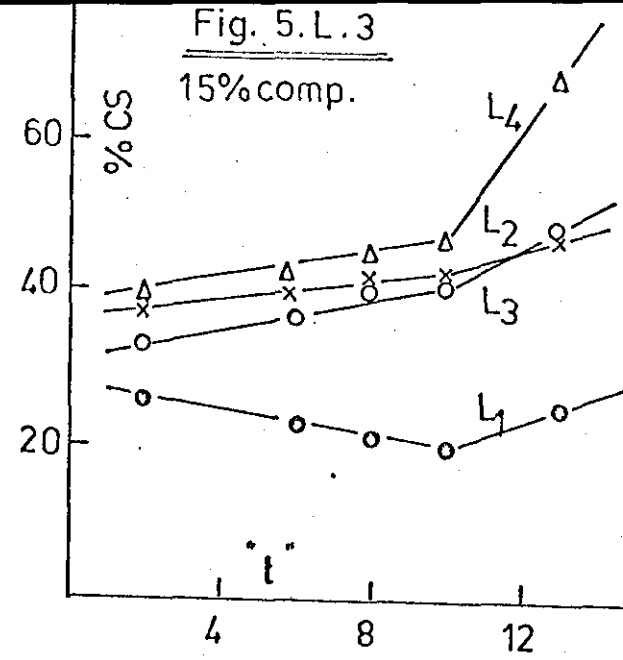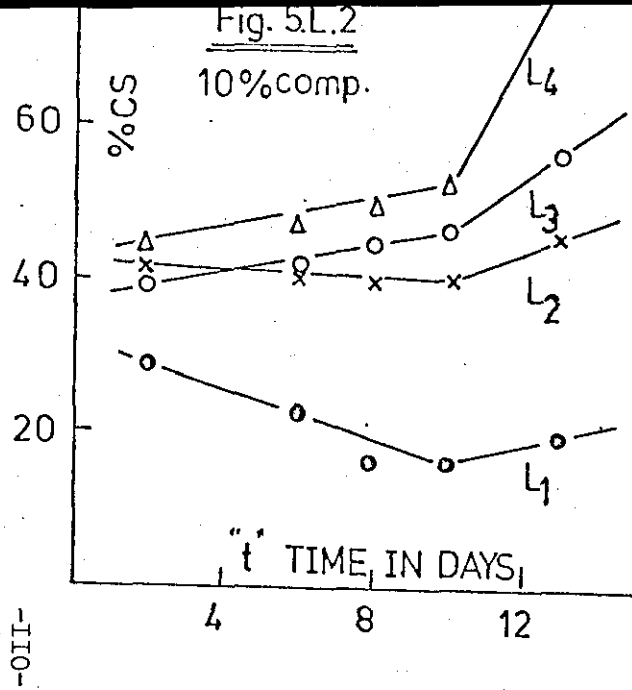
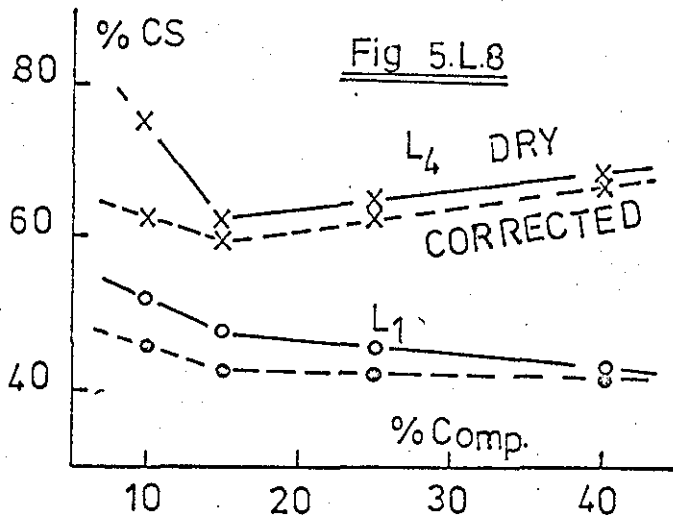Swelling under compressing strain for Series "L" mix.

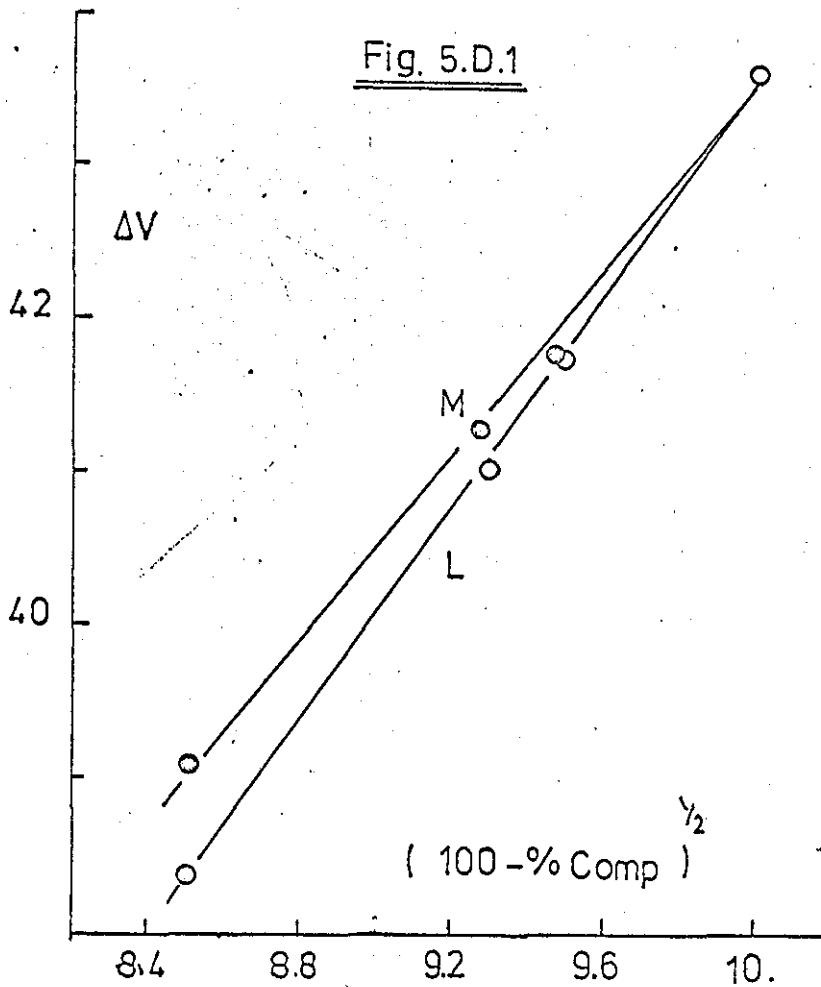Fig. 5.L.8. Relation between dry and corrected
swelling sets.

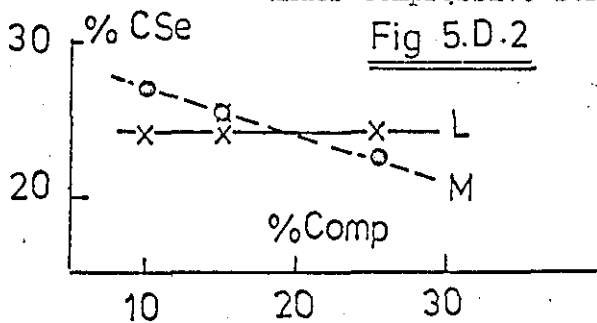Fig. 5.D.1. The effect of test piece size on swelling
under compressive strain.

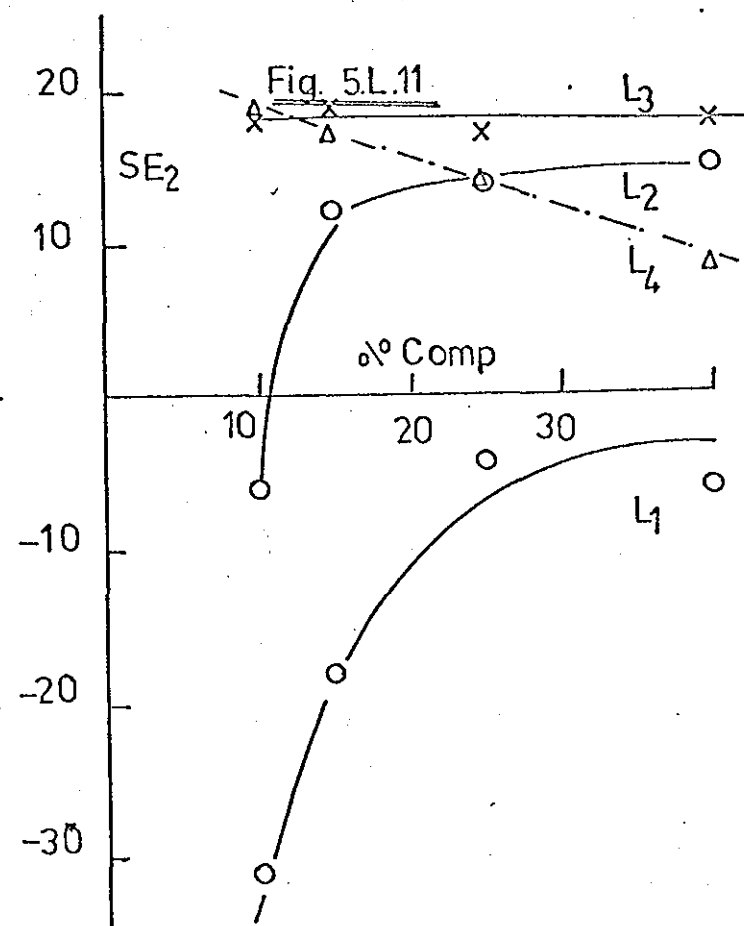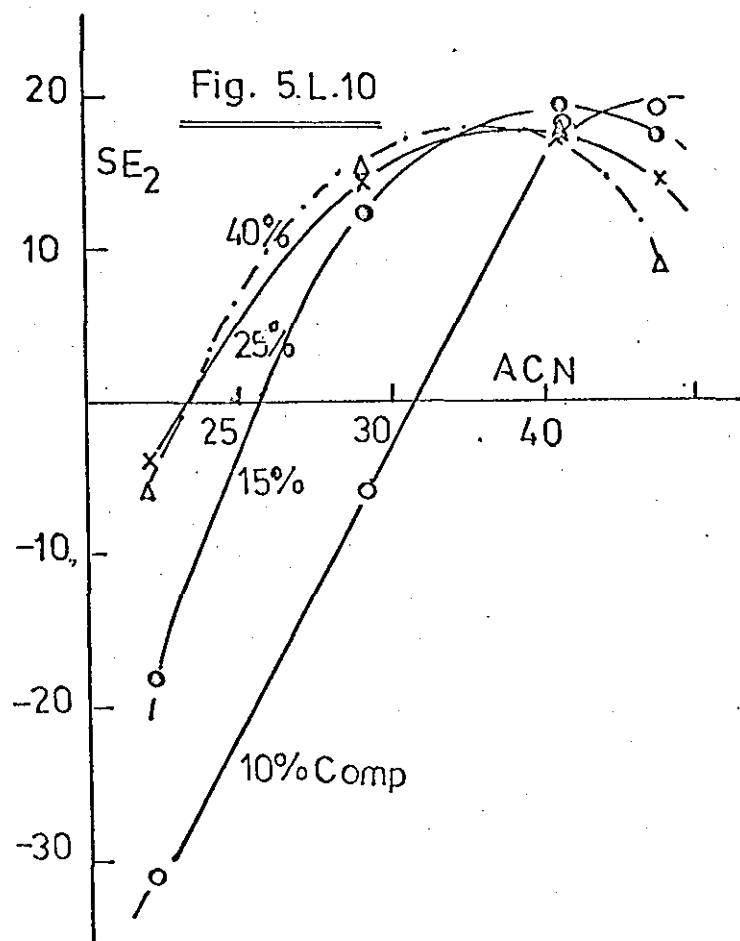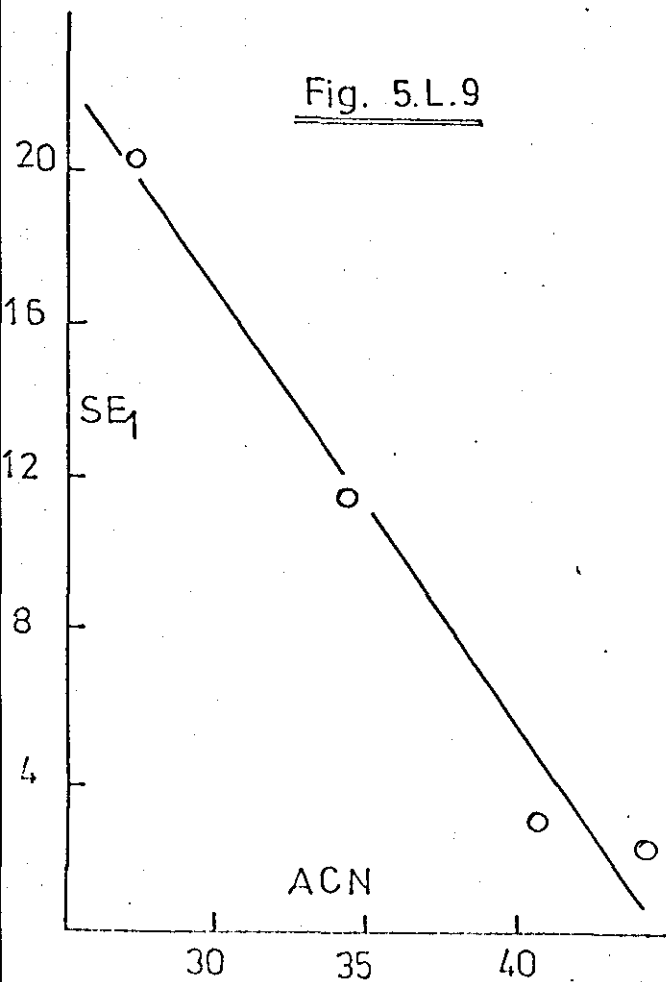Fig. 5.D.2. The effect of test piece size
on corrected sets.

Key to graphs: SE_1 Slope of ΔV_s vs $(100 - \%\text{compression})^{\frac{1}{2}}$.

SE_2 Slope of %CS vs Time in days .

Fig. 5.L.9

Fig. 5.L.10

Fig. 5.L.11

Section 6

CONCLUSION

The swelling of nitrile rubber vulcanisates by liquids can be reduced by increasing the amount of particulate filler and by reducing the particle size of the filler. Variation of the curing system and vulcanisation time will also affect, to a small extent, the amount of swelling. The selection of the acrylonitrile content depends on the solubility parameter of the polymer and the liquid. In case of mineral oils, the lower the acrylonitrile content, the higher will be the volume swelling.

The extraction of the soluble ingredients from rubber mixes must be considered. In the case of a l.b.l., preextraction of the rubber mix by the test liquids should be carried out before swelling measurements. These extractable matter depends on the liquid and degree of swelling produced.

With a particular oil, the relation between the equilibrium volume swelling and the penetration rate is linear, independent of the acrylonitrile content, and also of the type and amount of black.

The Flory-Rehner theory has been successfully applied to the results of swelling measurements of nitrile rubbers in organic liquids, reported above. It has to be noted that when μ is large equation (46) is extremely sensitive to small errors and solvents for which μ exceeds 0.7 cannot be used in calculating the crosslink density of rubber.

The cross-link densities (calculated from swelling) are consistently equal where the liquids are acetone and toluene but, differ in the case of chloroform. A reasonable explanation would be that the amount of extraction in case of chloroform is higher

-II3-

than the total volume extracted by acetone and toluene and
that chloroform attacks the rubber itself.

Making assumptions regarding the constancy of μ, which
appear to be supported by experimental evidence, the ratio of
the crosslink density values calculated from stress-strain and
volume changes for filled vulcanisates (G/G') is of interest
in being related to the black type more than to other factors
such as the acrylonitrile content, cure system, cure time and
black content.

The study has enabled the polymer-liquid interaction constants
to be determined for six polymers (one of them is the standard
nitrile rubber mix proposed by the technical panel of the
Association of Hydraulic Equipment Manufacturers) and eight
liquids (acetone, toluene, chloroform, n-hexane, n-heptane,
cyclohexane, n-butanol and formic acid) at room temperature $(20^{\circ}C)$.
The interaction constants for these polymers and seven oils $(ASTM_1,$
Tellus 27, $ASTM_{1,3}$, Stock 27, DTD 585, $ASTM_3$ and Stock 23) are
given at $100^{\circ}C$. It is to be noted that, where high swelling occurs,
the interaction constants change slowly with the change of acrylon-
itrile content of the polymer, but, where low swelling takes place,
μ changes rapidly. The interaction constant values usually decrease
with increasing the temperature, but the variation is not great. χ
The estimated values for μ agree well with those given by Bisio (1966).

Using liquids of known solubility parameters, it was possible
to calculate the solubility parameter of polymers. The method
used was the Bristow and Watson equation (50). This method is
more satisfactory than the method used by Shvarts (1957) and Sheehan
and Bisio (1966). Their methods has given a wide scatter of χ
results, from which arises a difficulty in drawing a representative
curve; in some cases, they give two curves, one for alkanes and

aromatic and the other for halogenated hydrocarbon (i.e. μ_s depends on the various chemical classes of liquids) leading to two values of solubility parameters.

A condensed table for solubility parameter of nitrile polymers obtained from this work and other investigators' works are given in Table 6.1.

Table 6.1 Solubility parameters of acrylonitrile copolymers

Butadiene/ acrylonitrile	δ_2 Lawandy 1973	Bristow & Watson δ_2 1958	δ_2 Bisio 1966	δ_2 Gee 1943	Scott & Magat δ_2 1949	δ_2 Small 1953	δ_2 Wilt 1954
100/0	8.25	–	8.32–8.60	–	–	–	–
82/18	–	8.73	9.35	–	–	–	–
80/20	9.20	–	–	–	–	–	–
75/25	–	–	–	–	9.50	9.25	9.45
72.7/27.3	9.64	–	–	–	–	–	–
72.2/27.8	9.63	–	–	–	–	–	–
70/30	–	9.87	9.65	9.38	–	–	–
65.6/34.4	9.88	–	–	–	–	–	–
61/39	–	10.42	9.9	–	–	–	–
59.3/40.7	10.3	–	–	–	–	–	–
55.9/44.1	10.57	–	–	–	–	–	–

The relation between the acrylonitrile content of the polymer and its solubility parameter has been shown to be linear. An extrapolation of this line to zero acrylonitrile content gives the solubility parameter of butadiene rubber (= 8.25). This plot can be used to find the solubility parameter of any butadiene acrylonitrile copolymer. The solubility parameters of the seven standard oils can be determined from an interchange of δ_1 and δ_2 in Bristow-Watson equation 50 to become:

$$\delta_2{}^2/RT - \mu/V = (2\delta_1/RT)\delta_2 - (\delta_1{}^2/RT) - \mu_s/V$$

and a plot of the solubility parameter δ_2 of the six polymers used before vs $\delta_2{}^2/RT - \mu/V$ enable the unknown δ_1 of the oils to be calculated. These values are given in the following table.

Table 6.2 Solubility parameters of oil

Name of oil	M.V.	S.P. δ_1
ASTM$_1$	649	8.32
TELLUS 27	414.6	8.42
ASTM$_{1,3}$	401.5	8.55
STOCK 27	376.5	8.60
DTD 585	331.7	8.65
ASTM$_3$	364.1	8.84
STOCK 23	341.3	8.92

It is to be noted from this table that the solubility parameter of these oils are higher than the expected values (compared with the swelling values of the same polymer and corresponding solubility parameters of low boiling liquids). This may be due to the relatively high molecular volume of oils.

Although there is extensive agreement that μ_s should lie within the range 0.3 to 0.5, the mean value of μ_s calculated (from the results given in Table 6.2 and equation 49) is 0.67. That is not surprising as some authors (Huggins 1943) have reported even negative values for μ_s.

It is obvious now to change the SCI system of oils given by AHEM to another system dealing with the solubility parameter of these oils. There is a linear relation between

the SCI of oils and the logarithm of solubility parameters of these oils ($\log \delta$). This can be shown in Fig. 6.1.

Plotting ΔV against $\log \delta$ for the four mixes 3, 4, 7 and 10 given by Blow (1970) has shown good linearity of the five points in every case, Fig. 6.2. In applying the same plot for pure gum mixes of the five polymers D_0, L_{01}, L_{02}, L_{03}, and L_{04} and seven oils given in Table (3.J.1.) the same linearity was obtained Fig. 6.3.

These linear relationships confirm that the SCI system can be replaced by another system dealing with the solubility parameters of oils.

The linearity of the relation between volume change and $\log \delta$ for any mix and a range of oils leads to a conclusion:

$$\log \delta = a \Delta V + b$$

where $a = \dfrac{\log \delta}{\Delta V}$ and b is the intercept of these lines with the axis reporting $\log \delta$.

The conclusion arises from the plot given in Fig. 6.2 that the slope of lines characteristic of acrylonitrile content of the polymer and that its position relative to $\log \delta$ axis is determined by the filler and plasticiser loading. The same conclusion can be extended to Fig (6.3) and it can be noticed that the interception points are almost the same. This is because the mixes have the same compounding formulas.

As this work contains numerical values of solubility parameters of polymers and oils and interaction constants of liquids and polymers, it is possible now to find out the volume change of a particular polymer in a particular liquid without any experimental work. The method can be summarised as follows:

i. having the solubility parameter of polymer and liquid and using $\mu_s = 0.3$ for low boiling liquids and $\mu_s = 0.67$ for oils the interaction constant μ can be calculated from the equation

$$\mu = \mu_s + V/RT \, (\delta_1 - \delta_2)^2$$

ii). From the plots of μ vs v_r (v_{ro}) Fig. (3.L.2.) for liquids and Fig. 3.J.1. for oils, v_{ro} of pure gum mixes can be calculated.

iii). The v_{rf} value for filled rubber can be obtained using Kraus equation:

$$v_{ro}/v_{rf} = 1 - \left[3 \, \phi \, (1-v_{ro}^{1/3}) + v_{ro} - 1 \right] c/(c-1)$$

where ϕ is a constant parameter having the values 1.363, 1.690 1.830 and 1.657 for FT, SRF, FEF and HAF black respectively.

The volume change of a particular polymer in a particular liquid can be found by a second method. This method can be summarised as follows:

i. The interaction constant μ can be calculated as given in the first method.

ii. The determination of G value from stress-strain measurement and using one of the equations 70, 71, 72 or 73 (section 4), G_o for pure gum mixes can be calculated.

iii. Using the equation

$$\ln (1 - v_r) + v_r + \mu v_r^2 = - \frac{\rho V}{G} \, (v_r^{1/3} - \tfrac{1}{2} v_r)$$

v_r can be obtained.

iv. Using Kraus equation v_{rf} for filled rubber can be obtained.

Kraus equation can be used to identify the type and amount of filler for a particular mix of nitrile rubber. The method can be summarised as follows:

i) having the amount of acrylonitrile content it is possible to know the solubility parameter (Fig. 3.L.4.) and the v_{ro} value for two liquids such as acetone and toluene can be obtained as before.

ii) the determination of the uptake of the two liquids (acetone and toluene) by the filled rubber can then be made.

iii) from the values of v_r for acetone and toluene we obtain two equations from which we can derive the value of ϕ. This parameter will identify the type of filler.

iv) Substituting in one of the equations the value of ϕ, the filler concentration (C) can then be obtained.

The kinetic theory of elasticity has been shown to be applicable to vulcanisates based on butadiene-acrylonitrile copolymers. The relation of G, for a rubber filled with carbon black, to G_o of the pure gum mix, is linear and given by the equation

$$G = G_o (1 - qC)$$

where q is a constant determined of the carbon black type. The values of q have been found to be 1.22, 2.17, 3.03 and 2.25 for FT, SRF, FEF and HAF respectively.

The data obtained for the moduli of vulcanisates with varying carbon black content do not fit the Smallwood equation (51) and Guth and Gold equation (52). A good agreement has been found with Guth equation $E = E_o (1 + 0.67\ f_s C + 1.62 f_s^2 C^2)$ in the case of thermal black taking the shape factor (f_s) of one (up to C = 0.35) and for FEF at a shape factor of three up to (C = 0.3). On the other hand, this equation does not fit

in the case of HAF and SRF blacks.

The relation between the volume swelling of test pieces under compressive strain ΔV_s and the value $(100 - \% \text{ compression})^{\frac{1}{2}}$ given by Blow et al (1969) has shown good agreement in the case of nitrile rubber at both low and high swelling values (A small increase can be obtained by the decrease of, black particle size and amount, the modulus and acrylonitrile content).

The diffusion of liquids into rubber is not changed by the different compressive strains.

The compression set of a test piece swollen to equilibrium increases with the increase of carbon black particle size and loading and also with the acrylonitrile content of the polymer. The slopes of the plots of set against time for various polymers in one oil differ dependent on the swelling and strain (Fig. 5.L.7).

There are different methods of identifying the acrylonitrile content of an unknown polymer:

1. The linear plot of swelling values of standard rubber mix vs the swelling values of unknown polymer mix in a range of oils. The slope of these plots can be used to identify the acrylonitrile content of polymer, Fig. 3.J.2,(3).

2. The plot of equilibrium volume swelling at different compressive strain vs $(100 - \% \text{ compression})^{\frac{1}{2}}$, Fig. (5.L.7).

3. The linear plot of the solubility parameter of polymer vs the acrylonitrile content of these polymers, Fig. 3.L.4.
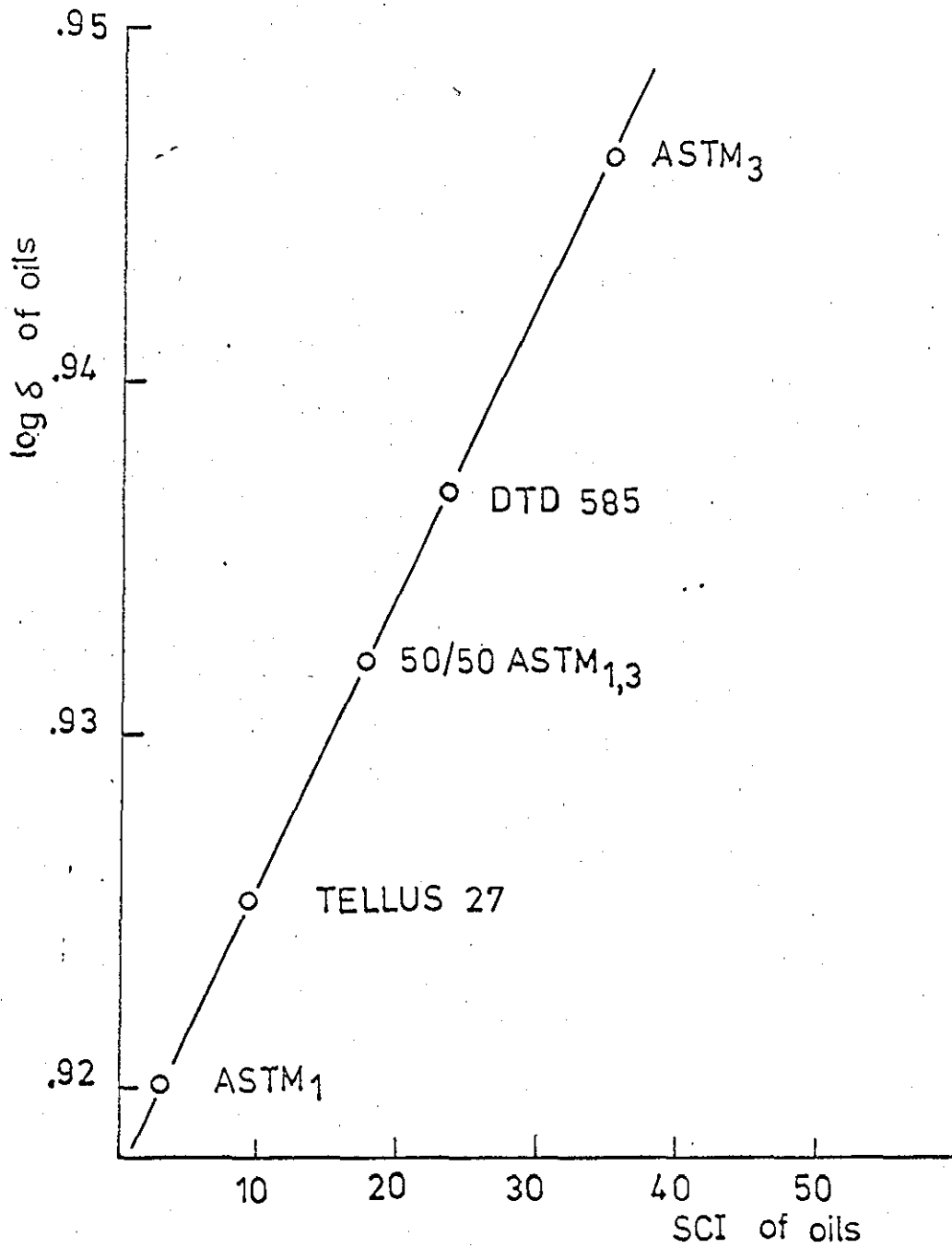
Fig. 6.1. SCI against log δ of oils.

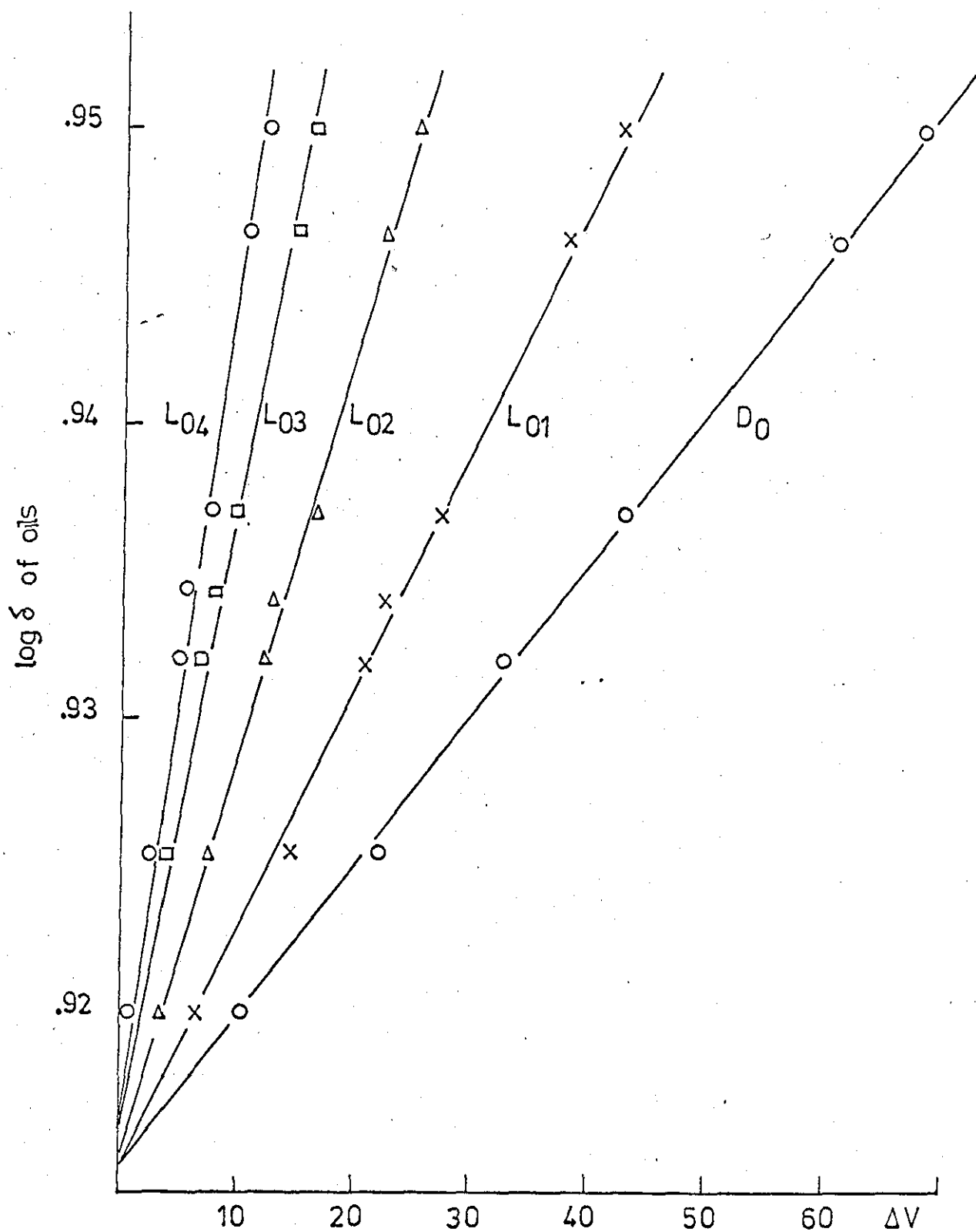Fig. 6.3. ΔV against log δ of oils. Pure gum mixes, data from tables 3.J.1 and 6.2.

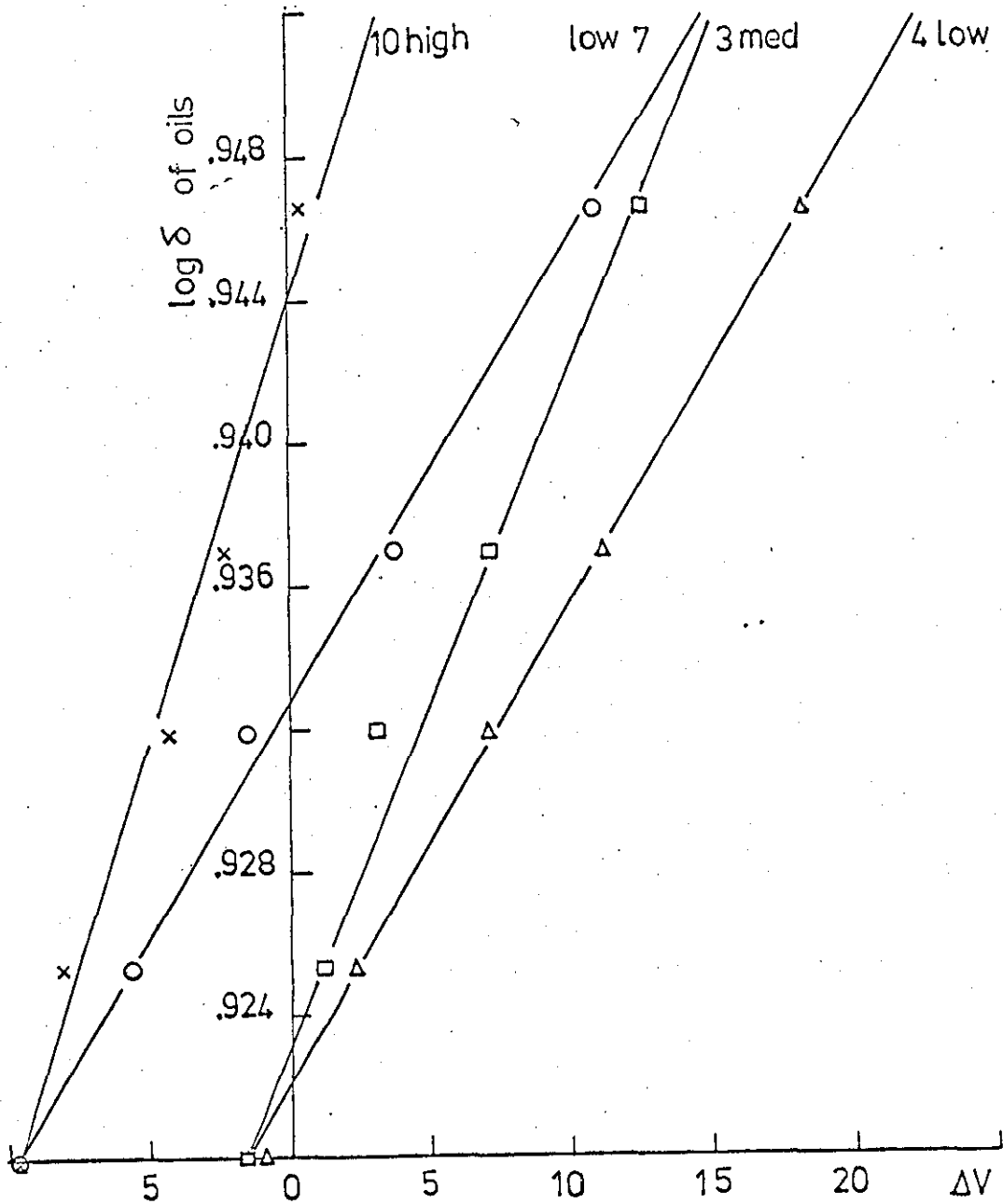Fig.6.2 ΔV against log δ of oils. From Blow,Rubber.Jnl.,152,5,37,1970
and table 6.2.

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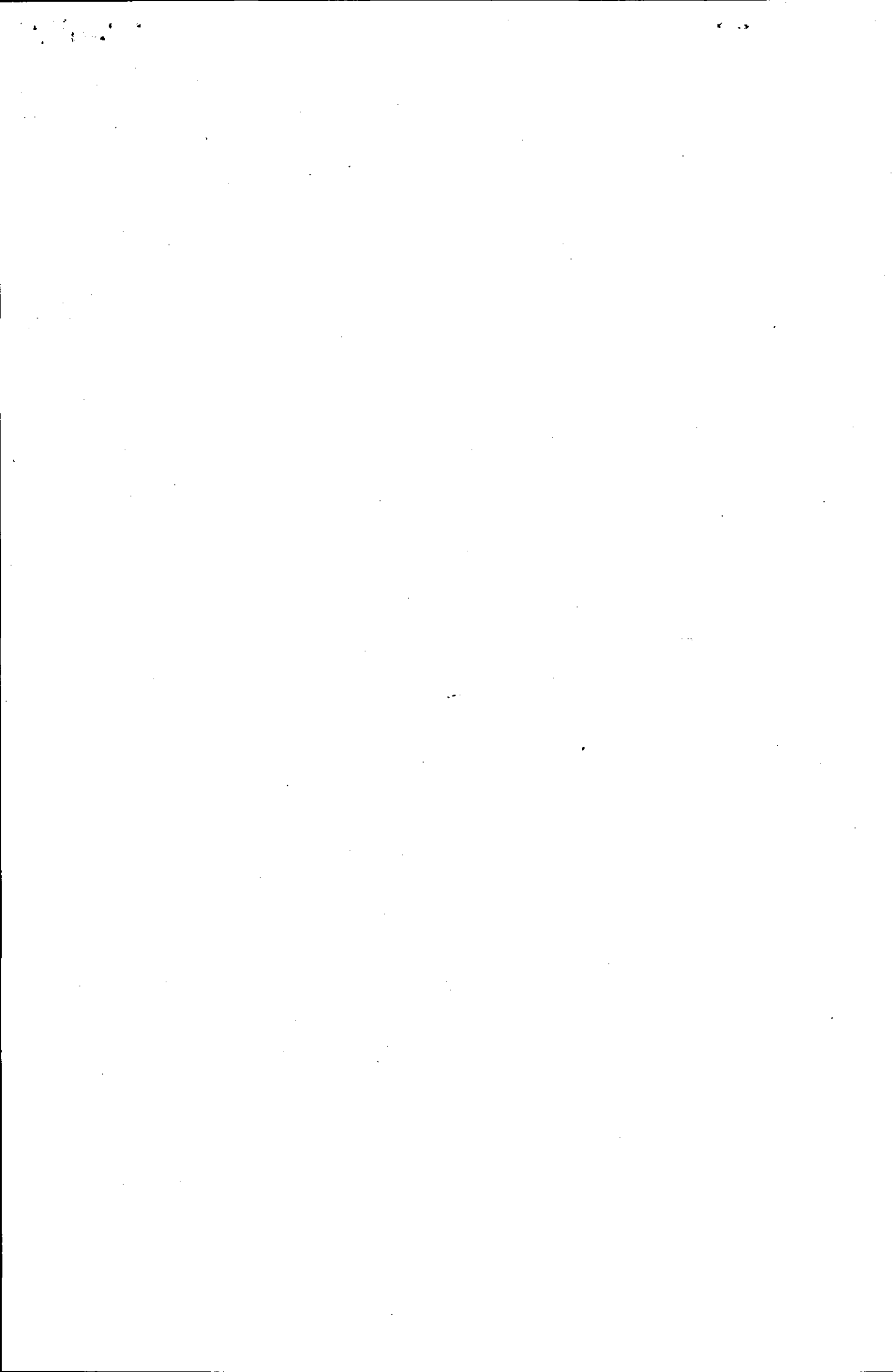
ABSTRACT

Swelling Behaviour of Nitrile Rubbers in Organic Liquids

Elastomeric seals are often used in contact with one of the many
types of organic liquids met in industry; it is desirable to invest-
igate the swelling of elastomers in the different liquids. One aim
is to arrive at a method of quantitative characterisation of rubber
mixes and organic liquids so that the volume change of a particular
mix in a particular liquid can be estimated.

A range of six nitrile rubbers with different acrylonitrile
contents, seven mineral oils of varying aromatic content and a
number of organic liquids having widely spread solubility parameter
values were used in this investigation.

The study involved rubber compounding variations as follows:
i) the acrylonitrile content of the polymer, (ii) the particle size
and structure of the carbon black filler, iii) the polymer content
iv) the vulcanisation system and v) vulcanising time.

Physical tests have been made on the unvulcanised and vulcanised
mixes.

The amount of liquid that is taken up by an elastomer is a
function of

i)   the relative cohesive energy densities (square of the solubility
       parameter) of the rubber and liquid.

ii)   the modulus of the vulcanisate which is related to the number of
       cross-links present and the filler content.

The net equilibrium volume change of a commercial vulcanisate
in a liquid is the uptake of liquid by the polymer content less the
volume of those ingredients which, being soluble in the liquid,
diffuse into it. To estimate these functions, swelling and tension

stress-strain measurements have been carried out on pure gum and filled vulcanisates. From these measurements the interaction constants for the different rubber/liquid systems have been calculated using the Mooney-Rivlin and Flory-Rehner relationships.

Having obtained the interaction constants and using values for the solubility parameters of the liquids reported in the literature, the solubility parameters of the various polymers can be obtained using an equation given by Bristow and Watson.

A series of vulcanisates was used to study the effects of the vulcanising system and vulcanisation time on the interaction constants. From these results it appeared reasonable to assume that the interaction constant for a particular mix and liquid is constant and to proceed to study the relation between the modulus of the vulcanisates and the corresponding volume fractions of polymer in the gels at equilibrium swelling. Two series of mixes filled with carbon blacks of differing particle size were used for this; one series of varying hardness and constant polymer content and the other of varying polymer content and constant hardness.

The conclusions to date may be summarised as follows:-

i)   The soluble ingredients of nitrile mixes are not fully extracted by mineral oils and solvents with low swelling power. There appears to be a relation between the amount of swelling and the amount of soluble ingredients diffusing into the oil.

ii)   As the acrylonitrile content of the polymer increases, the volume changes and the penetration rates in mineral oils decrease, with corresponding increase in the solubility parameter and modulus.

iii) The cure system has only a slight effect on volume swell, penetration rate, and interaction constant of the vulcanisate in a particular oil.

iv)   The cure time also has a small effect on the volume swell, but no effect on the interaction constant.

v)   Both the dry modulus of the vulcanisates and the volume fraction of polymer in the swollen gel are inversely proportional to the particle size of the carbon black and bear an approximately constant ratio to one another.

vi)   Mixes of the same hardness give similar values of swelling and modulus.

vii) No success was achieved to fit Einstein, Smallwood or Guth-Gold equations to the modulus results obtained from nitrile mixes with varying carbon black concentration and type, but useful empirical formula are given relating the network chain densities of pure gum mixes and filled rubber mixes to carbon black concentration.

viii) The kinetic theory of elasticity has been shown to apply to vulcanisates based on butadiene acrylonitrile co-polymers.

The effect of compressive strain on the volume change and set of the above mentioned rubber compounds has also been investigated. As the percentage compression strain increases the volume change decreases up to a certain limit of compression. A linear relation is obtained between the swelling values and $(100 - \text{percentage compression})^{\frac{1}{2}}$. The percentage set increases slowly with time initially and as the sample tends to reach equilibrium swelling, the percentage set rises steeply. The effect of strain on volume swelling and percentage set varies somewhat with polymer and black types and also the cure system.

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Elastomers for Seals.

Investigations concerned with the evaluation of elastomers for use as seals have, in the past, been confined very largely to determination of equilibrium volume changes in the liquid (usually at an elevated temperature to accelerate penetration), hardness changes and compression set at various temperatures in air. A limited amount of work has been published to show that, in sealing applications, other factors are important. These include:-

a) the rate of penetration of the liquid into the rubber and the balance of swelling of the polymer and extraction of soluble ingredients from the rubber by the liquid.

b) the effect of temperature and pressure on equilibrium volume change.

c) the effect of strain on the volume change.

d) the effect of constraining the rubber on the sealing pressures developed.

e) the stress retention in strained rubber both dry and in contact with the liquid.

Because of the wide use of mineral oil/nitrile rubber systems in hydraulics and lubrication, work should, at least initially, be carried out in this field.

Commercial mineral oils vary considerably in their composition which is seldom known to the rubber manufacturer who is asked to supply elastomeric seals. Some attempt should be made, therefore, by systematic selection to ascertain the effect of the known constituents of commercial oils in nitrile elastomers; systematic selection is required also of the elastomers to cover the variables of acrylonitrile content, filler type and quantity, plasticiser type and quantity and cross-linking system.

In addition to the routine testing of volume and hardness change and compression set, rates of penetration of liquid into the rubber and extraction of soluble ingredients should be determined both in the free state and under strain, to simulate the application of seals. Furthermore, cycling the seal/liquid assembly over temperature and pressure ranges to follow closely the liquid absorption and desorption and resultant sealing pressures will prove a profitable line of investigation.

The programme outlined above covers material variations on the one hand and newer, more sophisticated measuring techniques on the other. Some of the latter require only simple equipment but the introduction of pressurization and temperature cycling would involve the construction of special apparatus but this is unlikely to be of high cost.

C. M. BLOW.

9.7.70.

Notes on Results obtained by S. Lawandy, 1971-74.

Correlations:-

a. log δ (solubility parameter) vs. seal compatibility index for oils, but not dfr low boiling liquids; b. seal compatibility index vs. volume change - slope = ACN content -> solubility parameter; c. penetration rate vs. volume swelling; d. interaction constant vs. ACN content, large effect in case of heptane, hexane, cyclohexane - moderate effect toluene, acetone, formic acid, n-butanol - very little effect in case of chloroform.

Conclusions:-

a. interaction constant is not affected by cure time but is by cure system; b. extraction of ingredients is incomplete and is related to volume change; toluene extracts 25% less than acetone and chloroform 15% less; extractable content of series with varying vulcanising recipe vary widely, not unexpectedly; c. μ values:-

	ASTM 3	ASTM 1	cylcohexane	toluene
E_θ	.938	2.144	.78	.394
D_o			.797	.190
L_{o1}	.994	2.003	.989	.373
L_{o2}		2.671		
L_{o4}	1.751		2.859	.635
δ	8.84	8.32	8.2	8.9

Solubility parameters of oils fall between cyclohexane and toluene. Interaction constant of different polymers with oils and those with low boiling liquids are very different and serve to emphasise that, because molecular volumes are very different, the μ factor is different; d. relation of μ to ACN to be compared with Bristow and Watson - see plots; e. SCI vs. volume chnage for oils and low boiling liquids are different; f. C_1 value depends on cross-link density, filler type and proportion; volume change, v_{ro}, v_{rf} values depend on C_1 value, interaction constant (solubility parameter of liquid and polymer, molecular volume of liquid) and molar volume of liquid; g. fair agreement with Kraus values of ϕ - $v_{ro}/v_{rf} < 1$, decreasing with increasing volume of filler, decreasing with particle size, increasing with black structure; j. CMB's results showed that percentage of extractables by oil was dependent on degree of swelling or oil. Lawandy's L series suggest that, as effect is there for same oil, it is the degree of swelling that matters. More detailed analysis of CMB's results is required as some extractables will be more dependent on degree of swelling than others - e.g. plasticisers may come out at any degree of swelling, high molecular weight accelerators may only come out at high swelling. It appears that for 18-26% swelling, extraction is reduced by 25%, for 13-17 by 28%, for 8-12 by 30%, for 4-7 by35%. volume change of extracted or unextracted samples vs. amount of extract is linear for 5 oils in particular rubber, slope depends on ACN; volume change vs. percentage of acetone/toluene extract taken out by oil is linear for three ACN contents.

Effect on Elastomers of additives in liquids.

1. Work in 1940's by ICI on additives in aviation fuels.
   reported selective absorption of pyridine when present as
   an additive in fuel. No evidence from addition of aniline
   or monomethyl aniline to fuel of any selective absorption.

2. Lepera and Vogel (1968) - alcohol addition to diesel fuel.
   no indication of selective effects.

3. Eismann (Proc. N.C.H.I. <u>16</u>, 56, 1962) - mineral oil contamination
   of phosphate ester.

mineral oil %	0	2	5	10
swell %	5.9	12.2	23	42
(IIR L68h @ 70°C)		6.3	17.1	36.1
			15.7	34.2
				31.4

   no selective absorption as one would expect swell at lower
   % addition to be higher than anticipated from high % addition.
   opposite effect if anything.

4. Oronite - silicate ester fluid - fire resistant aircraft hydraulics.
   addition of 15% of ester (DOS ?) to increase swell or reduce
   shrinkage of CR mix.

5. CMB's work on swelling of series of NBR mixes in liquid paraffin and
   liquid paraffin plus 25, 50 and 75 % dibutyl phthalate. see IRI
   Brighton paper.

Areas for Further Work on Swelling.

1. Adjustment of SCI of oils - oil company interest; e.g. esters.
   cost, compatibility, effect on hydraulic and lubricating
   properties.

2. Effect of additives in oil on rate of penetration and rate and
   amount of extraction of solubles.

3. Volume changes on temperature cycling.