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Silicone rubbers: effect of silica fillers on processibility  
and properties

by

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## PREFACE

Although many people have contributed to this thesis all the work (excluding Appendices 1 and 2) was under my direction and the original ideas are mine: work at other Dunlop establishments was carried out at my request and, in some cases, with my assistance on experimental procedures.

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### 1.1 GENERAL BACKGROUND

To convert natural and synthetic rubbers into the rubber products so essential to modern society it is usually necessary to effect reinforcement and vulcanisation.

The former is normally achieved by the addition of a reinforcing filler, which has been defined by Boonstra (1971) as "a filler that improves the modulus and failure properties (tensile strength, tear resistance, and abrasion resistance) of the final vulcanisate". The latter, involving the joining together of polymer chains, either directly or via short chains of sulphur etc., is achieved through the action of a vulcanising agent; the resultant chemical bonds are known as crosslinks and produce a three-dimensional structure in the vulcanisate which imparts the desired elasticity to the rubber.

In some rubbers crystallites form on extension due to the rearrangement and orientation of the polymer chains: these act in some ways like reinforcing fillers and thus, for example, a natural rubber vulcanisate can exhibit high tensile strength in the absence of added filler; nevertheless even higher values are obtained in the presence of reinforcing fillers. Typical values of tensile strength are given in Table 1.1 in comparison with those for a nitrile rubber which is typical of a rubber which does not crystallise on extension: also given are values for

Table 1.1 Effect of fillers on the tensile strength (MPa) of peroxide vulcanised rubbers

Rubber \ Filler	Natural	Nitrile	Silicone
Nil	14.0	4.3	0.3
MT black	15.9	11.2	0.8
HAF black	19.3	20.1	7.0
Aerosil 300	22.3	24.4	4.9
Ratio $\frac{\text{HAF black}}{\text{Nil}}$	1.38	4.68	23.3

Filler volume concentration = 0.15

(Data from Southwart 1969 1)

a silicone rubber whose polymeric chains are so flexible that it is well-known for its outstanding low temperature performance. The low value of tensile strength of unfilled silicone rubber is one penalty to be paid for its good low temperature flexibility but it is to be noted that fillers have an increasingly advantageous effect as polymer flexibility increases, in the order natural rubber, nitrile rubber, silicone rubber.

Traditionally organic rubbers are reinforced with carbon blacks while silicone rubbers are reinforced with silicas; as a result the technological classification of fillers as reinforcing, semi-reinforcing, etc., as given with the data in Table 1.2, is not entirely consistent.

Besides the very good low temperature performance of silicone rubber already mentioned it vies with fluorocarbon rubber for resistance to high air temperatures: for inherent heat resistance as shown by compression set, it very nearly envelops all other rubbers (Blow 1964). It also has extremely good resistance to atmospheric conditions e.g. ozone, and is widely used in weather resistant seals e.g. in aeroplane window and door seals.

With these outstanding properties there is considerable incentive to overcome the inherent physical weakness of silicone rubber, as exemplified by tensile strength, so that it can make an even greater contribution to the output of the rubber industry.

Table 1.2 Typical filler types and properties

Classification	Type	Example	Particle size nm	Specific surface area m <sup>2</sup> /g
Reinforcing	Anhydrous Hydrated Aerogel	<u>SILICAS</u>		
		Aerosil 300	5-20	300
		Hi-Sil 233	22	150
		Santocel FRC	30	260
Semi-reinforcing	Calcined diatomaceous earth	Celite Superfloss	2,000-4,000	3.3
Non-reinforcing	Ground quartz	Minusil	10,000	1.4
Reinforcing	HAF black	<u>CARBON BLACKS</u>		
		Philblack 0	15-52	80
Non-reinforcing	MT black	Thermax	300-500	8

## 1.2 PROCESSIBILITY OF RUBBER-FILLER MIXES

Addition of fine particle carbon black to an organic rubber increases its viscosity leading to increased power requirement during mixing, and to an increase in mixing temperature which often necessitates the use of cooling water: dependent on the type of rubber there may be some partially compensatory reduction in viscosity due to mechanical scission of polymer chains.

On further addition of filler the mix eventually reaches a state where it will not accept any more - the mix has become "dry": this maximum concentration of filler decreases as the reinforcing power increases.

If the mix is not immediately processed e.g. calendered, its viscosity will increase further on storage and it may be necessary to remill it for a short time before subsequent processing.

Silicone rubber has a very low viscosity but this is increased by filler during mixing as in the case of organic rubbers; similarly there is a maximum volume concentration of filler which can be incorporated, varying approximately from 0.15 with Aerosil 300 to 0.37 with Minusil (Southwart 1969 1).

However there are two ways in which silicone rubber appears to be unique. Firstly it is often necessary to allow a few weeks to elapse between mixing and subsequent processing and vulcanisation for optimum physical properties to be attained by the vulcanisate (Servais

and Riley 1961): this storage is known as bin-ageing.

Secondly, there is a very much bigger increase in viscosity during bin-ageing than in the case of organic rubbers and it is possible for a silicone rubber-silica mix to develop a pseudo-vulcanised state in which milling increases the tendency for the mix to crumble. This phenomenon is known variously as crepe-hardening, crepe-ageing or structuration and can even occur during initial mixing.

Even in a mix which is not crepe-hardened the remilling necessary to reduce the viscosity to an acceptable level for further processing can take an hour or more, with very obvious cost penalties in a production process.

In practice the increase in viscosity is minimised by the use of antistucture agents e.g. diphenyl silanediol (Peter, Knopf and Noll 1957) or by surface treatment of the silica (General Electric Company 1958): it is, however, often still necessary to bin-age mixes. With the practical success of these two methods of preventing, or reducing, the stiffening of silicone rubber-silica mixes the basic reaction remained substantially uninvestigated until Southwart and Hunt (1968) attempted to quantify the changes in the processibility of simple mixes of silicone rubber and silica by measurement of the time taken to remill them to a viscosity suitable for further processing.

### 1.3 BOUND RUBBER

It has been known for a long time that interaction between carbon black and natural rubber, whether in solution or in a conventional rubber mix, leads to insolubilisation of some of the rubber, first called bound rubber by Fielding (1937).

W F Watson (1954) showed that milling, of a dried mix of carbon black added to natural rubber in solution, rapidly increased the bound rubber; he attributed this to the action of free radicals produced during the milling. Similar effects were obtained with silica (W F Watson 1954), although Wake (1954) doubted that free radicals were responsible in that case. J W Watson (1956) showed that bound rubber was directly proportional to carbon black surface area.

Later Wagner and Sellers (1959) studied the kinetics of bound rubber formation of styrene-butadiene rubber and butyl rubber with carbon black and silica and obtained similar activation energies for each combination (approximately 0.08 MJ/mol), thus indicating chemical reactions: they also explained the ability of silica to accept free radicals.

Warrick and Lauterbur (1955) obtained similar effects with silicone rubber and silica and attributed the reactions to the siloxane bond rearrangement earlier discussed by Patnode and Wilcock (1946). On the other hand Baker, Charlesby and Morris (1968) attributed similar bound rubber

at least in part, to condensation reactions: they recorded higher values of bound rubber with silica than with a similar particle size carbon black.

Southwart and Hunt (1968) investigated the dependence of bound (silicone) rubber on silica concentration, bin-ageing time and reprocessing and confirmed that bound rubber increased during bin-ageing. They found that mixes could crepe-harden with less than 40% of their rubber bound yet be processible with nearly 100% of their rubber bound: they concluded that rubber was bound in two forms, only one of which gave a three-dimensional structure to reduce processibility.

The author later showed that the time taken to extract all the soluble silicone rubber was itself dependent on bin-ageing time and could be in excess of 28 days (Southwart 1969 2).

Although the swelling of a vulcanisate is widely used for the determination of the density of crosslinks it is comparatively rarely used to investigate the bound rubber of a rubber-filler mix.

J W Watson (1956) found that bound rubber and swelling were linearly related in a series of natural rubber-carbon black mixes. The author reported similar relationships for silica in nitrile rubber and for silica in silicone rubber; in the latter case values fell on the line irrespective of immersion time (Southwart 1969 1).

Endter and Westlinning (1957) found differences in swelling of natural rubber gels even when two silicas of comparable particle size produced similar amounts of bound rubber. Blow (1973) in his review of bound rubber reported his own investigation of similar differences in carbon black - natural rubber mixes and included an estimation of the rigidity of the swollen gels.

In an earlier review of bound rubber Gessler (1969) concluded that butyl rubber and carbon black reacted strongly "in a vulcanisation-like process" to give a "shell" of highly restrained rubber around the carbon particles together with "bound rubber bridgehead chains which connect one carbon particle to another".

Although the author's own terminology changed during the work to be described it is proposed to use only the definitions first given in his own review (Southwart 1971):

Adsorbed rubber	—	polymer segments immobilised in the immediate vicinity of filler particles, whether by orientation on the filler surface or by entrapment in filler agglomerates.
Interparticular rubber	—	polymer segments joining filler particles to give effective cross-linkages, and (interlocking) polymer loops attached to filler particles.
Matrix rubber	—	polymer free of interaction with filler.

The adsorbed rubber is synonymous with the "shell of rubber" described by Gessler and others, while the interparticular rubber is synonymous with Gessler's "bound rubber bridgehead chains".

In these terms the results described above were interpreted as follows (Southwart 1969 2):-

1. Interaction between polymer and filler produces adsorbed rubber and interparticular rubber.
2. Bound rubber is the sum of adsorbed rubber and interparticular rubber.
3. Interparticular rubber leads to a reduction in processibility.
4. Swelling is dependent on relative proportions of adsorbed rubber and interparticular rubber.

#### 1.4 AIMS

The discovery that the well-known stiffening of silicone rubber-silica mixes (culminating in some cases in crepe-hardening) was reversible raised a hope that more detailed investigation of the phenomenon would lead to commercial exploitation.

The study of unvulcanised mixes would clearly give an insight into their processibility but would also provide further evidence of polymer-filler interaction to test the concept of adsorbed rubber, interparticular rubber and matrix rubber.

Having confirmed that the reversibility of stiffening was not a unique property of one particular silicone rubber the principal aim was to investigate the interaction between silicone rubber and filler in various ways so that the resultant structures could be analysed and controlled.

Bound rubber has often featured in studies of reinforcement but has normally depended on an assumption of constant rate of extraction of soluble rubber: in some cases such an assumption is erroneous (Southwart 1969 2). Particular attention has therefore been paid to the rate of extraction of silicone rubber from unvulcanised mixes and comparison made with the rate of extraction from unfilled silicone rubber vulcanisates.

The effect of time was also chosen for particular study due to its commercial importance in a number of ways. The extra cost of long mixing or milling times has already been referred to: bin-ageing of mixes is expensive due to the cost of the necessary storage space, while production planning is complicated by this enforced delay between mixing and subsequent processing: ideally a production mix should give consistent performance however long it is stored, particularly in a unit where small quantities may be required at infrequent intervals.

Although it has been known for a long time that some properties of a rubber-filler mix change on storage, much published work has ignored this fact, as recently regretted

by Blow (1973). As it appeared that these effects were greater for silicone rubber-silica mixes than for organic rubber-carbon black mixes it seemed likely that the proposed investigation would provide a contribution to the wider subject of the particulate reinforcement of rubbers if other fillers and rubbers were included for comparison.

Only a minority of previously published studies of particulate reinforcement of rubbers had been concerned with simple unvulcanised mixtures of rubber and filler; indeed it has been suggested that reinforcement occurs principally through vulcanisation ( J W Watson 1956). As a crepe-hardened silicone rubber-silica mix behaved in some ways like a vulcanisate it was clearly exhibiting reinforcement without the complication of vulcanising agents and vulcanisation. However the final commercial product is usually vulcanised so some measurements have been made on vulcanisates.

Processibility has been assessed by the previous milling technique, with investigations of various types of silicone polymer and silica, and of the effects of temperature and additives.

A wide range of physical properties has been measured but principally the bound rubber, swelling and heat of melting of unvulcanised silicone rubber-silica mixes and the stress under various strain conditions of various rubber-filler mixes, both vulcanised and unvulcanised.

Further physical properties have been determined on the same or similar mixes, by workers at Dunlop Research Centres in Birmingham and Canada; this work is described in Appendix 1.

Some theories of reinforcement are reviewed in Appendix 2.

The aim of this thesis is to present the results obtained, to interpret them in terms of adsorbed rubber, interparticular rubber and matrix rubber, and to assess their relative importance in controlling the processibility and physical properties of silicone rubber. The secondary aim is to consider their relevance to the broader issue of the particulate reinforcement of rubbers.

Separate chapters are devoted to the main topics of processibility (Chapter 3); effects of immersion in organic liquids (Chapter 4); properties involving stress-strain relationships (Chapter 5); heat of melting (Chapter 6); and miscellaneous physical properties (Chapter 7). At the end of each of these chapters, and in Appendix 1, conclusions are drawn from the data presented in them.

For a clearer picture of the effect of reinforcing fillers, however, it is necessary to consider the data collectively. This is the aim of Chapter 8, for various aspects ranging from the effect of silica in unvulcanised silicone rubber, to properties of the vulcanised rubber-filler system.

In the final chapter further conclusions are presented, on the processibility and properties of the silicone rubber-silica system, and on reinforcement theory. Possible areas for further research are outlined.

## CHAPTER 2 EXPERIMENTAL MATERIALS AND METHODS

### 2.1 POLYMERS

The silicone rubbers were all commercial materials obtained from Imperial Chemical Industries Limited and were representative of the types available: three of these were low shrinkage versions i.e. devolatilised to reduce the loss otherwise occurring during the customary commercial high temperature post curing of vulcanisates. The chemical compositions were as follows:

- E301 dimethyl polysiloxane (low shrinkage)
- E302 methyl vinyl polysiloxane (high shrinkage)
- E303 methyl vinyl polysiloxane (low shrinkage)
- E351 methyl phenyl vinyl polysiloxane (low shrinkage)

The phenyl and vinyl concentrations were of the order of 5 and 0.5 mol % respectively (Pierpoint 1967) but no attempt was made to determine these concentrations.

Also used was a dimethyl polysiloxane oil (MS 200) obtained from Midland Silicones Limited (now Dow Corning Limited): this had a stated viscosity of 30,000 cSt, equivalent to a molecular weight of nearly 80,000 (Midland Silicones Limited 1964).

Various batches of the polymers were used and in some cases their molecular weight was determined before use, or following extraction from a mixture with filler, using the same intrinsic viscosity apparatus and

procedure as Severn (1969) for solutions in Analar toluene. The MS 200 was found to have a molecular weight of  $0.1 \times 10^6$ .

In some cases a weighed portion of rubber was heated in a tared Petri dish (50 mm diameter) in an oven and subsequently cooled in a desiccator over concentrated sulphuric acid, to determine the weight loss (%).

An approximate thickness of 2.5 mm was used and this was obtained by allowing a suitable quantity of polymer to flow to constant thickness at room temperature.

In the case of filled mixes a disc (diameter 50 mm) was cut from 2.5 mm thick sheet (Section 2.3): the loss in weight was again expressed as a percentage of the original polymer.

The organic rubbers were as follows:

natural rubber	pre-masticated pale crepe
nitrile rubber	Krynac 801: a copolymer of butadiene and approximately 38 mol % acrylonitrile, obtained from Polysar (UK) Limited.

## 2.2 FILLERS

Some of the fillers used are given in Table 1.2 with nominal values for ultimate particle size and specific surface area. Similar details, where available, for other fillers used, are given in Table 5.6: EP 154 is Aerosil 300 surface treated by Imperial Chemical Industries Limited to render it hydrophobic.

In some cases the moisture content was determined by the loss in weight (%) of a portion heated for at least 2 hours between 150° and 250°C and then cooled in a desiccator over concentrated sulphuric acid.

The specific surface area of some silicas was determined using the rapid method developed by Sears (1956) in which a suspension of the silica in aqueous sodium chloride is titrated between pH 4 and pH 9 with 0.1 N sodium hydroxide. Sears found empirically that the specific surface area of the silica  $S$  ( $m^2/g$ ) as determined by the nitrogen adsorption method (BET) of Brunauer, Emmett and Teller (1938) was linearly related to the titre  $V$  (ml) of 1.5 g of silica by the equation:-

$$S = 32 V - 25 \quad . . . .(1)$$

Difficulty was experienced in establishing the necessary equilibrium conditions at pH 9 but it was eventually found possible to obtain satisfactory agreement, on silicas with BET specific surface area as determined by Severn (1969), provided that the silica weight was reduced to 1 g.

Later the method was simplified by using a non-equilibrium titration end point for easier use as a routine control test for silica (Appendix 3): values obtained were less than BET values but adequate for their purpose: correlation is expected when the equation has been

modified empirically for samples of known specific surface area (BET).

### 2.3 PEROXIDES AND VULCANISATION CONDITIONS

For the determination of some physical properties a sheet, approximately 175 mm x 175 mm x 2.5 mm, was prepared in a frame mould in a single daylight electrically heated hydraulic press under a pressure of approximately 8 MPa.

Unvulcanised sheets of silicone rubber and natural rubber were prepared by moulding at room temperature; unvulcanised sheets of nitrile rubber were prepared by moulding for 10 minutes at 110°C.

Vulcanised sheets of silicone rubber-silica mixes were prepared by moulding for 10 minutes at 110°C after addition (normally) of 1.5 parts (weight) per hundred parts (weight) of rubber (phr) of a mixture of equal parts (weight) of 2, 4 dichlorobenzoyl peroxide in an unspecified low molecular weight polysiloxane: this is commercially available as Perkadox PDS-50 from Novadel Limited.

Vulcanised sheets of silicone rubber-furnace black mixes were prepared by moulding for 10 minutes at 171°C after addition of 1.95 phr of a mixture of equal parts (weight) of 2, 5 dimethyl 2, 5 di (t-butyl peroxy) hexyne-3 and an inert base: this is commercially

available as Luperco 130XL from Wallace & Tiernan Incorporated via Kingsley and Keith (Chemicals) Limited.

Vulcanised sheets of other mixes were prepared by moulding for 10 minutes at 150°C after addition of 1.5 phr of dicumyl peroxide (95 percent minimum purity), commercially available as Dicap R from Hercules Powder Company Limited.

Where it was desirable, or necessary, to use other concentrations of any of these peroxides the concentrations are given with the results.

#### 2.4 OTHER MATERIALS

A small sample of morpholine, the inner anhydride of diethanolamine, was obtained from Dunlop Research Centre, Birmingham. It is a strongly basic liquid and a powerful siloxane condensation catalyst.

Also obtained from Dunlop Research Centre, Birmingham was a small sample of 1, 1-diphenyl-2-picrylhydrazyl (DPPH), the well-known free radical scavenger (Charlesby 1960) used by W F Watson (1955) in natural rubber.

Various organic liquids were used to extract soluble rubber and swell insoluble rubber: wherever possible Analar or similar high purity grades were used.

## 2.5 MIXING

Usually approximately 100 g of silicone rubber was banded, under atmospheric conditions, on a two-roll rubber mill (230 mm x 100 mm and friction ratio 1.08). The appropriate filler was then added in stages and mixing was continued until adequate dispersion appeared to have been achieved: the mix was then sheeted off the mill at a thickness, normally approximately 3.0 mm, appropriate for subsequent tests.

Mixes were generally bin-aged on a laboratory bench to simulate production conditions: the duration of this storage being known as bin-ageing time (BAT). Zero BAT signifies that physical properties were determined almost immediately after making any necessary test sheet, and usually within one hour of removal of the mix from the mill.

Peroxide, when required, was added on the same mill after adequate dispersion of all other ingredients.

## 2.6 PROCESSIBILITY

To assess the processibility of a mix after bin-ageing approximately 100 g was returned to the mill. Often on the first pass through the nip the mix crumbled but eventually it began to soften, cohere and finally band on the mill rolls. Milling was continued until the sample attained a level of processibility deemed adequate for technological use: the total time taken, in minutes, was called the breakdown time (BDT). In any one experiment

successive BDT were determined on the same sample except where stated otherwise.

Sometimes a sample continued to crumble on the mill and showed no signs of softening within 30 minutes: this was then considered to be crepe-hardened. Mixes with BDT recorded in excess of 30 minutes were distinguished by some softening having occurred within the 30 minutes.

As far as possible all processing was performed under constant conditions of mill nip, temperature, operator, and operator's speed of working. Several operators have been accepted after satisfactorily completing a number of trial mixes: no attempt has been made to differentiate between their respective results.

The viscosity of some silicone rubber-silica mixes was determined on a Wallace-Shawbury Curometer (Mark 6) obtained from H W Wallace and Company Limited. Constant volume pellets were cut from sheet using the specimen cutter provided and inserted in the platen cavity at 100°C: the height of the trace on the recorder chart was noted after operation for 10 minutes at an appropriate stroke adjuster setting number, and recorded as amplitude (mm). No attempt was made to calibrate the Curometer as only a comparative assessment of viscosity

was required. At maximum amplitude (200 mm) the movement of the paddle was approximately 0.4 mm.

## 2.7 IMMERSION IN ORGANIC LIQUIDS

### 2.7.1 Bound rubber

Various methods have been employed for the determination of bound rubber defined as the percentage of the original gum not extracted by toluene under specific immersion conditions: occasionally other organic liquids were employed.

The bound rubber value was usually obtained by allowing the liquid to evaporate at room temperature from the swollen gel to constant weight which was assumed to consist of the original filler plus the bound rubber.

Normally approximately 0.4 g portions were placed in approximately 25 ml of fresh toluene several times during a determination, sometimes with determination of the bound rubber at the time of changing the toluene.

### 2.7.2 Swelling

The absorption of liquid was usually determined concurrently with the bound rubber and could therefore be used to calculate the weight % of liquid absorbed by that bound rubber. This is the swelling used in the previous work (Southwart 1969 2), but is now

designated  $S_B$ .

The liquid absorbed, equal to the difference in weight between swollen gel and dried gel, was sometimes expressed as the weight of liquid per 100 parts (weight) of the total original mix ( $S_M$ ) or as the weight per 100 parts (weight) of polymer initially present in a mix ( $S_P$ ).

The volume of liquid absorbed per 100 parts (volume) of bound rubber ( $V_B$ ) was sometimes calculated from observed weights using published values of density of rubber and liquid.

### 2.7.3 Osmotic pressure effect

Weighed portions (approximately 0.4 g), or similar portions previously immersed in toluene, were immersed in toluene (25 ml) containing 0 to 20 weight % of E303; after the appropriate immersion period the swollen test-pieces, and the solutions, were dried at room temperature. The product of the rubber weight/solvent weight in the final solution and the weight of toluene in the gel per 100 parts (weight) of original polymer in the test-piece was calculated. This was equal to the expression  $S'_S T_2/T_3$ , against which the measured bound rubber (G) was plotted to determine the partition coefficient (P) and "true" bound rubber (B) (Section 11.4).

## 2.8 STRESS-STRAIN MEASUREMENTS

### 2.8.1 Young's modulus

Two methods were employed for the determination of Young's modulus; both used strips cut from the prepared sheets

using a specially manufactured cutter with a sliding blade. Two bench marks were applied approximately 100 mm apart, using suitably colored ink; their actual separation was determined using a travelling microscope reading to 0.01 mm. The thickness of the test strip (approximately 2.5 mm), and its width (approximately 11.5 mm), were determined at several points using a dial gauge also reading to 0.01 mm: mean values were used for the subsequent calculation of Young's modulus.

In the first method a test strip was suspended vertically, weights were added to a pan attached to the bottom of the strip and the distance between the bench marks was determined using the travelling microscope. Weights were normally added at approximately 3 minute intervals until creep was observed. Sufficient samples have however been left for longer periods to confirm the absence of creep i.e. increase in length with time under constant load, at strains approaching 0.2 in gum vulcanisates and 0.01 in silicone rubber containing high concentrations of Aerosil 300, whether unvulcanised or vulcanised.

At low strains silicone rubber exhibited Hookean behaviour as shown by the mean values (of quadruplicates) plotted in Figure 2.1, for an unvulcanised mix of E303 and 32 phr of Aerosil 300. On the first extension there was no further increase in length when the load was maintained for 1 day, 3 days and 1 day at strains of approximately 0.003, 0.006 and 0.010 respectively. The slope of the

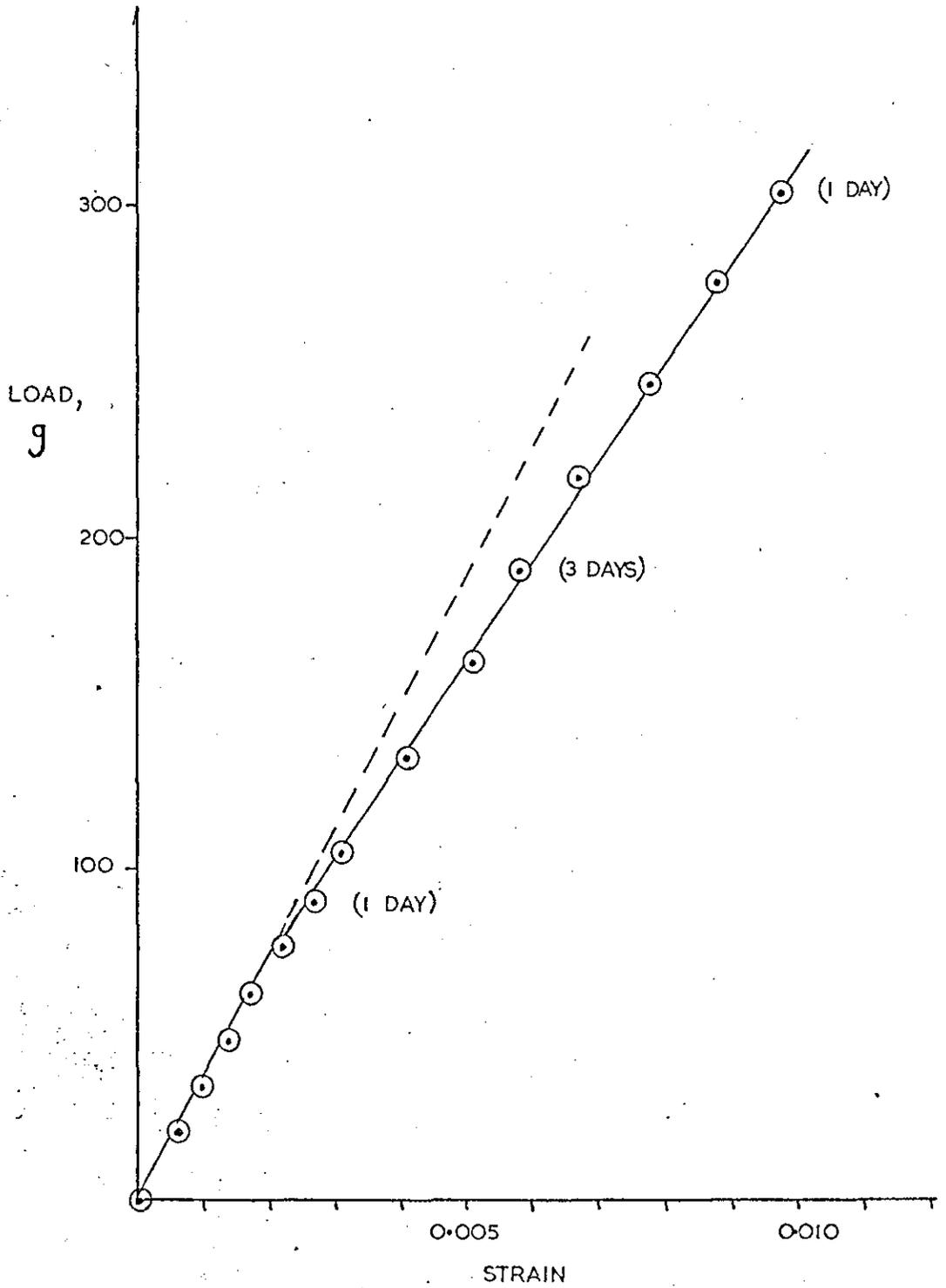


Figure 2.1 Relationship between load and strain (quadruplicate mean) for E303 containing 32 phr of Aerosil 300 (load maintained for stated time)

line changed at a strain of approximately 0.002; a similar change was detected in other test-pieces when measurements were adequately replicated.

On a single extension up to the strain at which creep occurred, values were usually interpreted as falling on a single line, as shown in Figure 2.2, for the values from the origin to a strain of approximately 0.01. The slope of a similar line, on a load-extension plot, was used, with the test-piece dimensions, to calculate Young's modulus.

In the second method strips were extended at 25 mm/min on a recording, tensile testing machine, after recalibration of the load sensing circuit of a proof ring transducer to the low loads required (maximum sensitivity 5N full scale deflection). As the time axis of the recorder was proportional to extension the load-extension curve was plotted on the recorder after taking up any slack in the sample. Plots were usually linear from the origin up to the extensions at which creep was observed in the first method and gave values of Young's modulus in reasonable agreement with the previous ones.

### 2.8.2 Yield stress

Both the stress and the strain at which onset of creep denoted the departure from truly elastic behaviour, were found to be dependent on bin-ageing time. However it was found that the addition of constant load increments

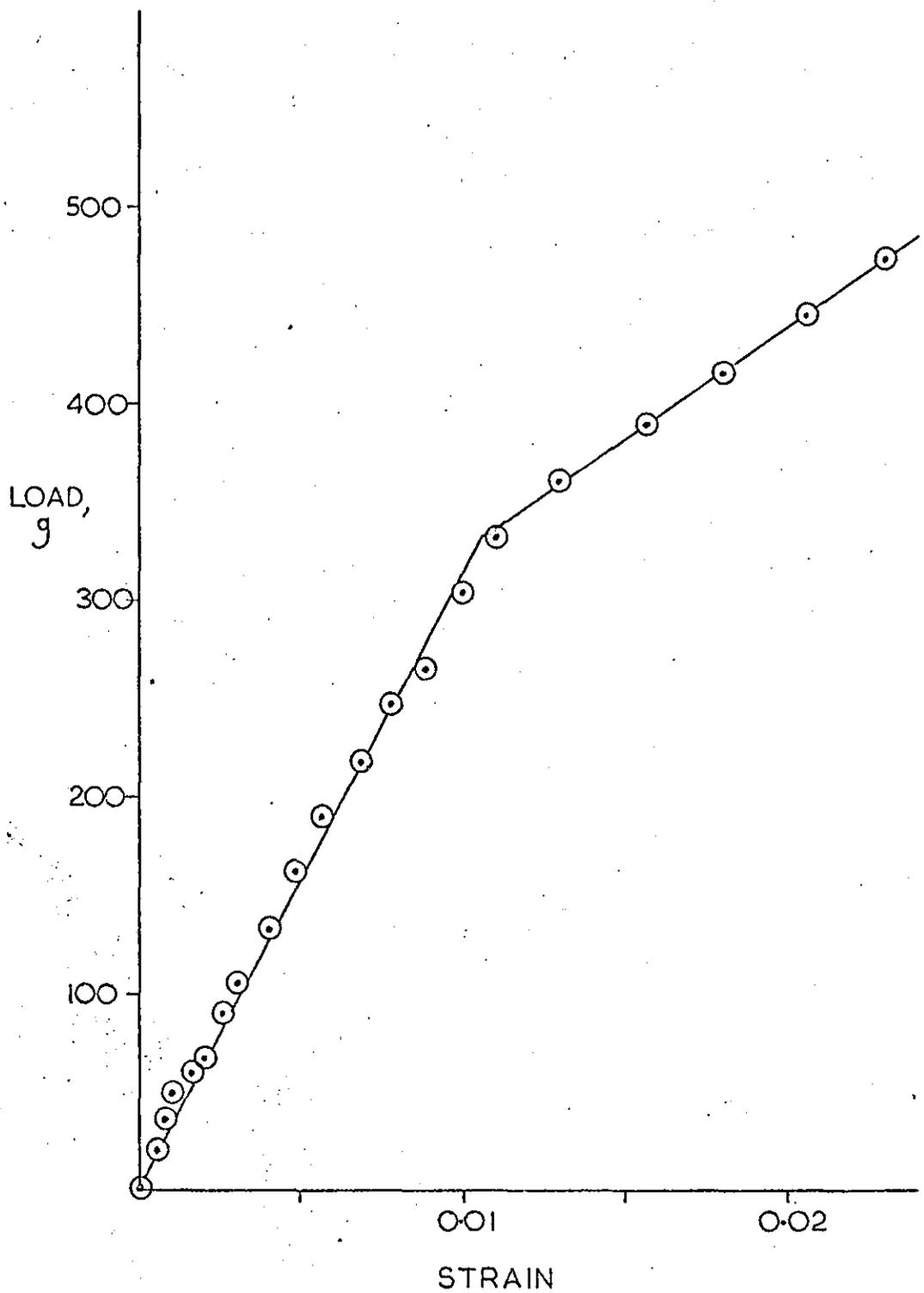


Figure 2.2 Interpretation of data from Figure 2.1 if not replicated. For strains  $> 0.01$  see Section 2.8.2

at constant time intervals, usually 5 minutes, to a test strip used for the first method of determining Young's modulus gave a further linear region; as shown in Figure 2.2 on further loading of the test strip from Figure 2.1.

The load at the intersection of the two straight lines was related to the original cross-sectional area of the test strip for the calculation of the stress; this was designated the yield stress.

#### 2.8.3 Stress at higher extension

Stress-strain curves at higher extensions up to break were determined on the tensile testing machine, normally using dumb-bells (BS 903 : Part A2 : 1971) cut from the moulded sheets: after calibration of the load sensing circuit to a suitable sensitivity, test-pieces were extended at 500 mm/min: elongation was measured using a hand-held ruler and marked as appropriate on the recorder chart by depressing a switch to alter the electrical input signal momentarily.

#### 2.8.4 Compression modulus

The stress-strain relationship was also determined in compression using an instrument purchased from H W Wallace and Company Limited. This (Reticulometer) is similar to a standard Micro hardness tester but with the indenter and loading system modified so that the load on the test-piece cut from the sheet, approximately 2 mm x 2 mm, can

be applied over the whole surface, and varied. The version used was Servo-operated and the deflection was automatically indicated on a dial gauge which, allowing for the inherent strain amplification in the instrument, allowed changes in test-piece thickness to be determined to the nearest 0.01 mm.

Usually this instrument is used for the determination of the load-deflection characteristics of swollen vulcanisates and it is recommended that test-pieces be pre-stressed with the maximum load to be applied; the resultant plot is normally curved at very low strains but values of compression modulus are calculated from the linear region at slightly higher strains, the initial curvature being attributed to poor contact between the loading device and the test-piece (Smith 1967).

To permit comparison with the values in extension no pre-stressing was used in the current work. Curvature was still apparent in the load-deflection plot but the first few points often appeared to be on another straight line, through the origin. To magnify the deflection for those low strains two test-pieces were cut from the same cylinder, approximately 6 and 12 mm in height and 11 mm in diameter. The data obtained on compression, to strains of approximately 0.2, are given in Figure 2.3 and confirm the initial linearity but this is surprisingly independent of test-piece height: the slope of the second linear region is inversely proportional to test-piece height and therefore a true indication of the modulus

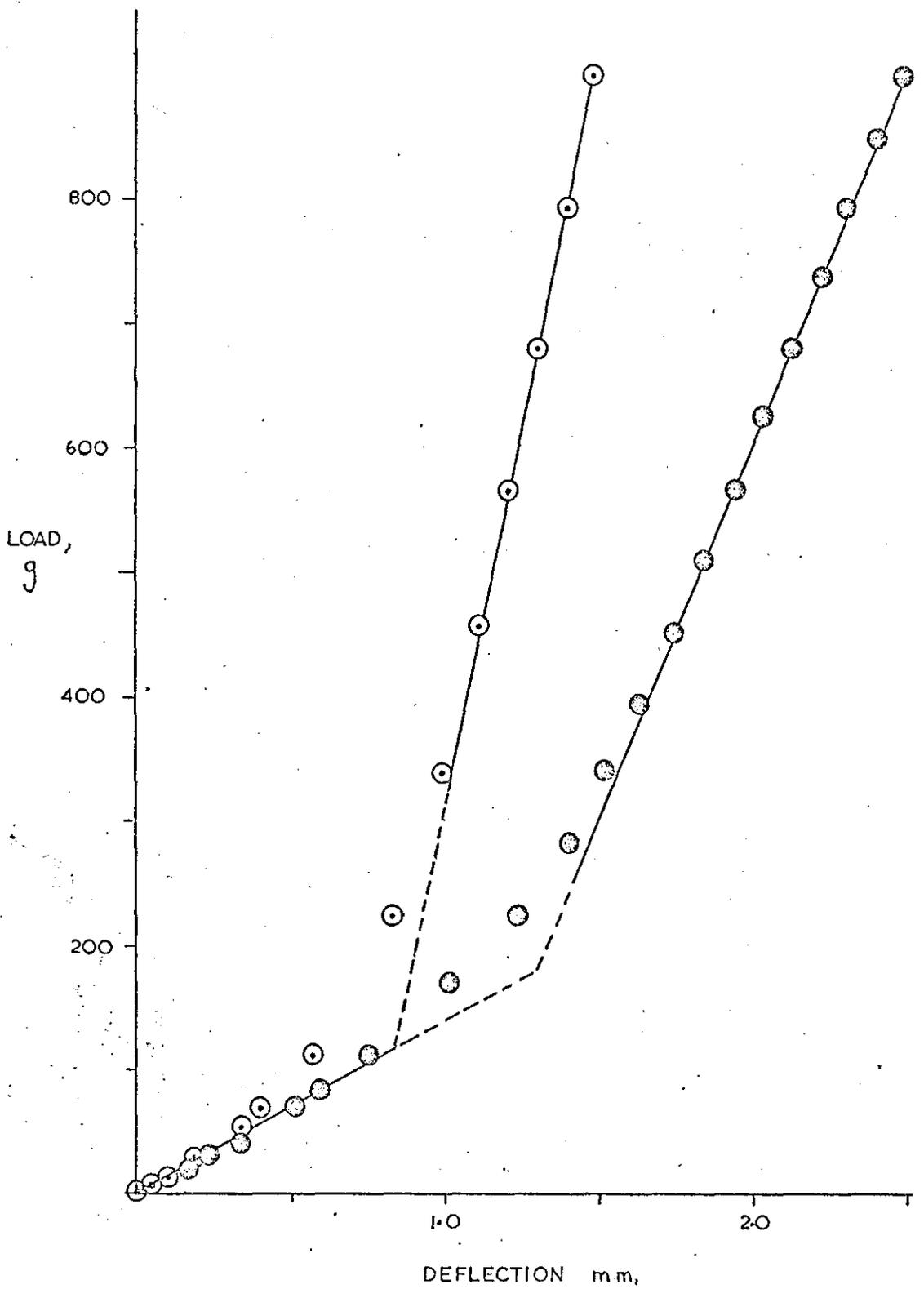


Figure 2.3 Dependence of the relationship, between compressive load and deflection of a silicone rubber-silica vulcanisate, on approximate test-piece height

(○ 6 mm ● 12 mm)

of the material. Generally compression modulus was calculated from the slope in that second region but sometimes it was calculated from the slope in the first linear region; in both cases the slope of the line was multiplied by one third of the original test-piece height/original cross-sectional area.

#### 2.8.5 Hardness

As a general rule apparent hardness was determined by the method of BS 903: Part A26 : 1969, on 2 plies of portions of a moulded sheet using a standard Dead-load hardness tester for rubber purchased from H W Wallace and Company Limited.

Occasionally it was also determined by the microtest of BS 903: Part A26 : 1969, on single portions of moulded sheet using a standard Micro hardness tester for rubber purchased from H W Wallace and Company Limited.

#### 2.9 HEAT OF MELTING

Small portions, up to 40 mg, were weighed into preweighed aluminium cups, also fitted with preweighed aluminium lids when measurements were not completed within one operating session. One cup containing the test portion was placed on the rear platform of a Differential Scanning Calorimeter fitted to a Du Pont 900 Differential Thermal Analyser; an empty cup, and lid when appropriate, was placed on the front platform as a reference.

Samples were generally cooled to approximately  $-100^{\circ}\text{C}$  by addition of liquid nitrogen to a container fitted to the top of the calorimeter, over which was placed a bell jar supported to leave a small space at its base for the escape of gaseous nitrogen, thus reducing the tendency for the sample and reference to be vibrated off the calorimeter platforms: this technique gave a cooling rate of approximately  $20^{\circ}\text{C}/\text{min}$ . The liquid nitrogen container was then removed, the normal calorimeter covers fitted and the instrument programmed to give a heating rate of  $10^{\circ}\text{C}/\text{min}$ . The melting endotherm, peaking at approximately  $-36^{\circ}\text{C}$ , was recorded and its area was calculated by counting squares after drawing in a suitable baseline; no correction was made for the non-linearity of the indicating thermocouple for comparison of heats of melting but allowance was made to the indicated temperature of the melting peak.

In some cases samples were quenched by direct immersion in liquid nitrogen followed by transfer to a precooled calorimeter, while in others the rate of cooling was programmed to  $10^{\circ}\text{C}/\text{min}$ .

Two Analysers and various calorimeters were used but no significant comparison of their respective sensitivities was made.

Melting endotherm area was reproducible within  $\pm 4\%$  over a short but variable period, as shown by the values in Figure 2.4 for E302 containing 32 phr of Aerosil 200 where those on the line were obtained in one session; values obtained at other times deviated more from the line but gave good agreement between replicates: on average, values were directly related to test-piece weight. Neither reproducibility nor linearity were affected by the presence of filler, or by the rate of cooling provided this was constant throughout a series of determinations.

To concentrate determinations into the minimum possible period melting endotherms were calculated per unit weight of polymer content, instead of as a fraction of the melting endotherm of silicone rubber itself. Results are expressed in the arbitrary units of chart area per unit rubber content ( $\text{in}^2/\text{g}$ ).

#### 2.10 REBOUND RESILIENCE

Rebound resilience was measured on a Dunlop Tripsometer borrowed from Dunlop Limited, Polymer Engineering Division. It was operated according to BS 903 : Part A8 : 1963 except that the measurements were made at room temperature.

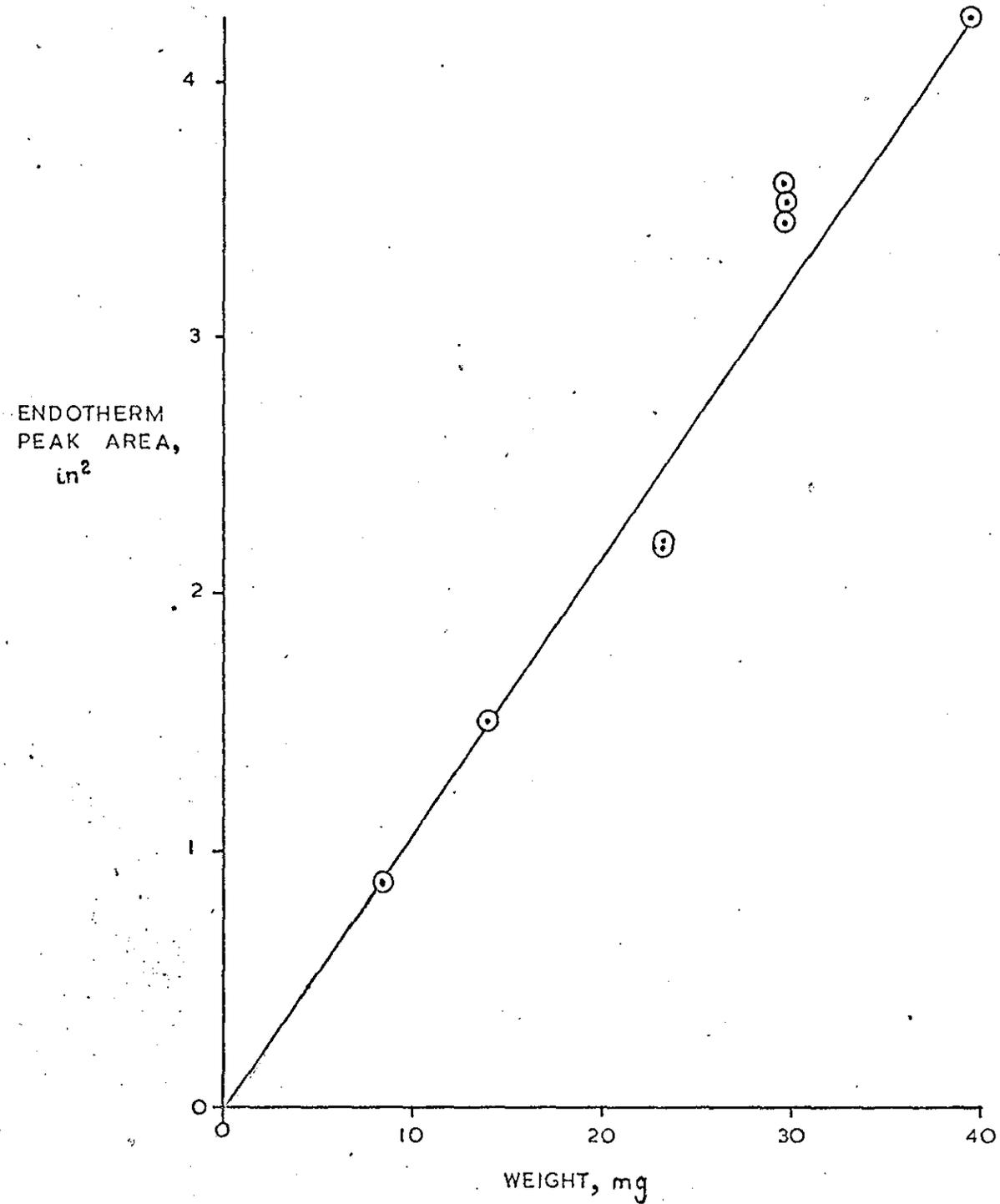


Figure 2.4 Dependence of the chart area, of the melting endotherm of E302 containing 32 phr of Aerosil 200, on the test-piece weight

## CHAPTER 3 PROCESSIBILITY

### 3.1 EFFECT OF SILICONE RUBBER TYPE

The breakdown times in Figure 3.1, of various silicone rubbers containing 32 phr of Aerosil 300 taken from one homogenised batch, established that the decrease in processibility (increase in breakdown time) on bin-ageing, <sup>shown by the solid symbols,</sup> and the increase in processibility (decrease in breakdown time) on successive remillings (after the first one or two), <sup>shown by the open symbols,</sup> were not unique to the E302 used originally by Southwart and Hunt (1968).

The magnitude of the change in processibility, and the dependence on bin-ageing time, were not independent of rubber type and only E303 exhibited the eventual increase in processibility due to bin-ageing alone observed in the previous work.

Similarly the breakdown times in Figure 3.2 confirmed that the acceleration of the changes by elevation of the bin-ageing temperature was again not unique to E302 (Southwart 1969 2). They also indicated that the eventual increase in processibility on bin-ageing was a general phenomenon but with the rate of change dependent on rubber type. They further established the disappearance, on bin-ageing, of the tendency for the breakdown time of the second remilling to be higher than that of the first remilling.

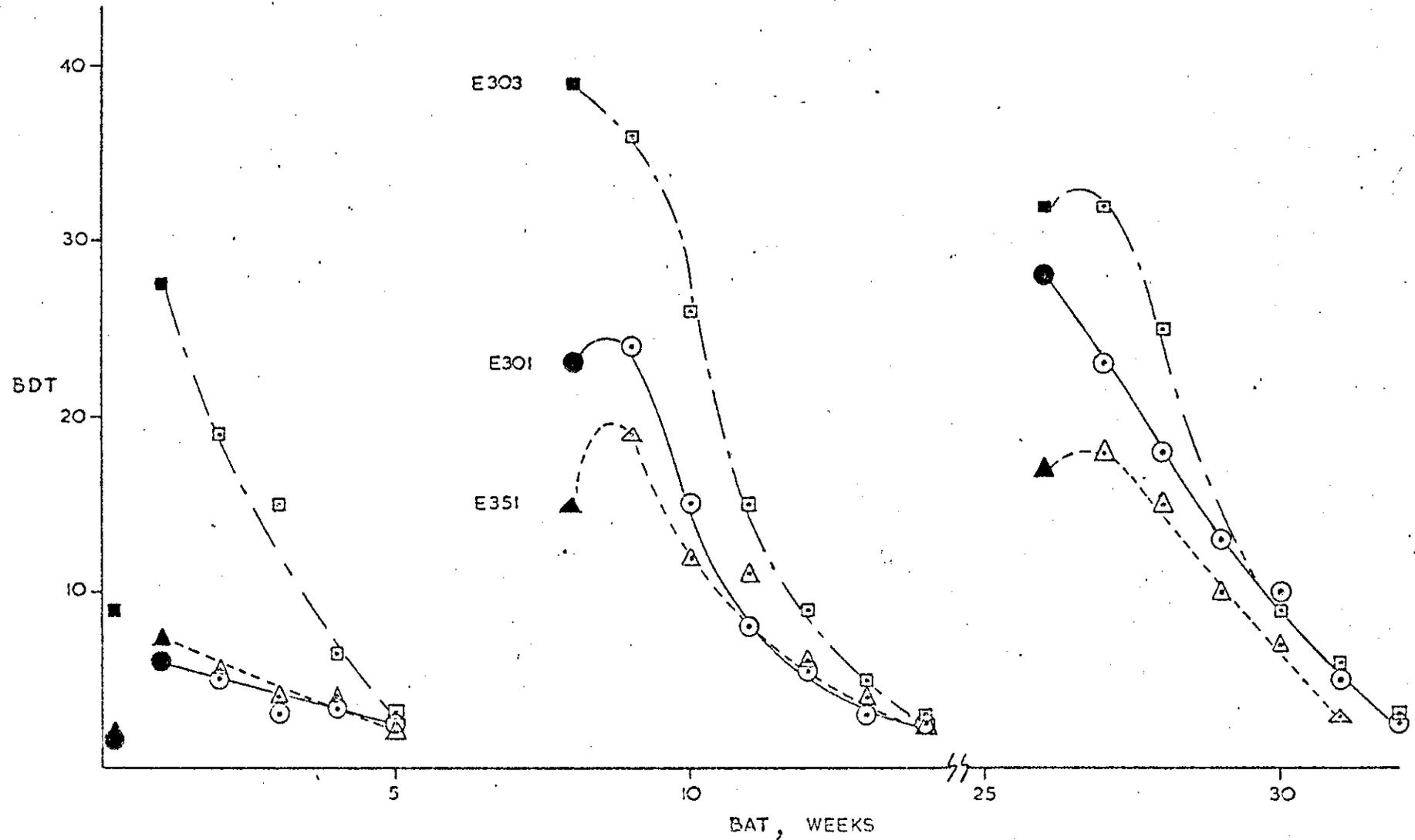


Figure 3.1 Effect of bin-aging time (BAT) at room temperature, remilling and silicone rubber type, on the breakdown time (BDT) in the presence of 32 phr of Aerosil 300

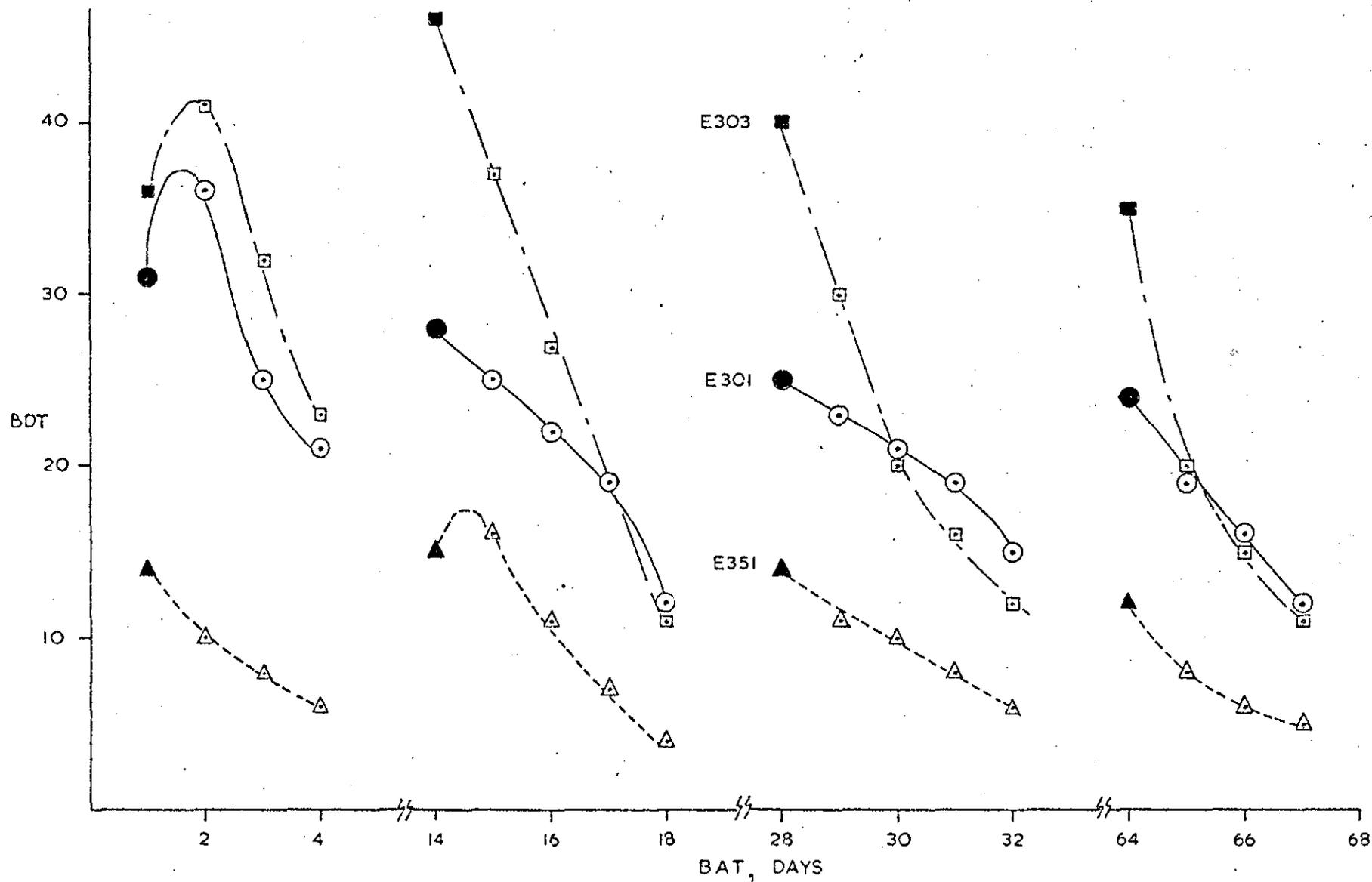


Figure 3.2 Effect of bin-ageing time (BAT) at 70°C, remilling and silicone rubber type, on the breakdown time (BDT) in the presence of 32 phr of Aerosil 300

The breakdown times in Figure 3.3 revealed larger and more rapid changes in processibility of E302 with lower molecular weight ( $0.47 \times 10^6$ ) than normal ( $0.9 \times 10^6 \pm 0.1 \times 10^6$ ) in the presence of 32 phr of Aerosil 300.

### 3.2 EFFECT OF TEMPERATURE

The breakdown times in Table 3.1 confirmed the increase in the rate of change of processibility on increase of temperature; in this case E303 containing 32 phr of Aerosil 300 was heat treated for 4 hours at temperatures between 150 and 305°C immediately after mixing, but it was bin-aged at room temperature.

For a very crude estimate of reaction kinetics the time to maximum breakdown time for E303 and Aerosil 300 was estimated as 4 hours at 200°C (Table 3.1), 12 days at 70°C (Figure 3.2) and 56 days at room temperature (21°C) (Figure 3.1); logarithm of rate constant plotted (Figure 3.4) against the reciprocal of temperature (K) gave an approximate activation energy of 0.038 MJ/mol. This was between the 0.013 MJ/mol quoted by Thomas (1966), for polymer solvation, and the 0.08 MJ/mol of Wagner and Sellers (1959), attributed to chemical reaction between polymer and filler (Section 1.3).

### 3.3 EFFECT OF MIXING TIME

The breakdown times in Table 3.2 revealed that increases in mixing time of E303 and 32 phr of Aerosil 300 could lead to a maximum similar to those sometimes obtained on remilling (Figures 3.1 and 3.2).

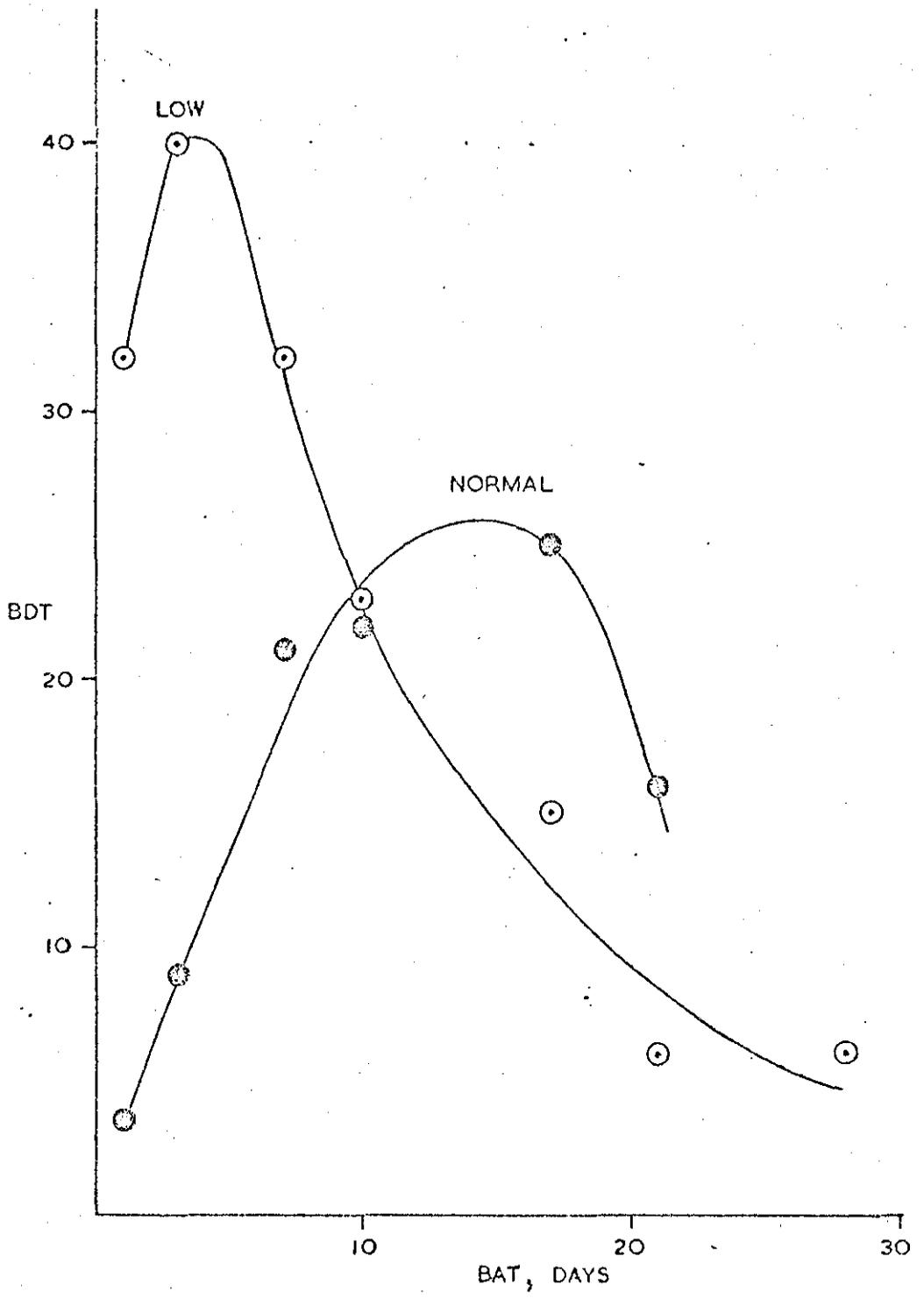


Figure 3.3 Effect of molecular weight on the relationship between breakdown time (BDT) and bin-ageing time (BAT) at room temperature for E302 containing 32 phr of Aerosil 300 (LOW -  $0.47 \times 10^6$  NORMAL -  $0.83 \times 10^6$ )

Table 3.1 Effect of heat treatment for 4 hours on breakdown time, min

Heat treatment temperature	Bin-ageing time at room temperature	
	3 days	10 days
150°C	21	44
200°C	39	54
250°C	25	24
305°C	approx 20	9

E303 containing 32 phr of Aerosil 300 (different batches)

Table 3.2 Effect of mixing time on breakdown time

Mixing time, min	Breakdown time, min
30	20
42	28
60	15

E303 containing 32 phr of Aerosil 300

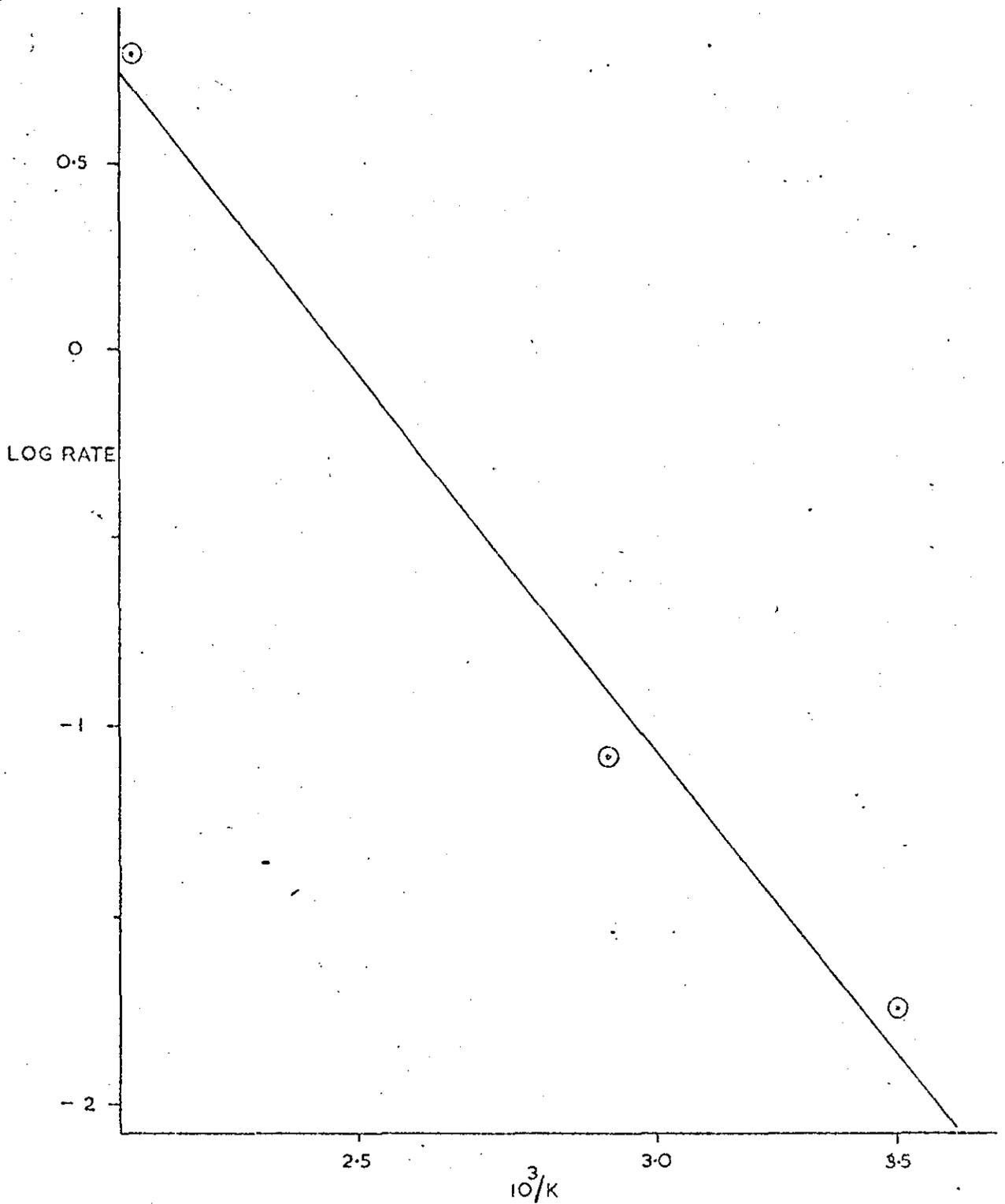


Figure 3.4 Arrhenius plot of estimated reciprocal days to maximum BDT, and storage temperature (K) for E303 containing 32 phr of Aerosil 300

### 3.4 EFFECT OF FILLER CONCENTRATION

Breakdown time increased with increase of filler concentration but the time to maximum breakdown time generally decreased. These effects are shown by the breakdown times in Figure 3.5 for E302 containing Aerosil 300, bin-aged at room temperature: however, the mix containing 40 phr of filler crepe-hardened within 3 days of mixing.

### 3.5 EFFECT OF FILLER TYPE

Although all fillers increase the viscosity of silicone rubber only the "reinforcing" fillers were found to have an effect on the processibility as determined by breakdown time and this effect increased with increase of specific surface area, except when the filler had been treated, as mentioned in Section 1.2. Some typical breakdown times are given in Table 3.3 for E303 mixtures containing 32 phr of filler, bin-aged at 70°C; the value recorded for the mix containing Celite Superfloss is a measure of the time taken to band the material and does not imply even a small decrease in processibility compared with the polymer itself.

When bin-ageing was at room temperature the breakdown time of E303 containing 56 phr of EP 154 rarely exceeded one minute thus further demonstrating the relatively small effect of this filler on processibility.

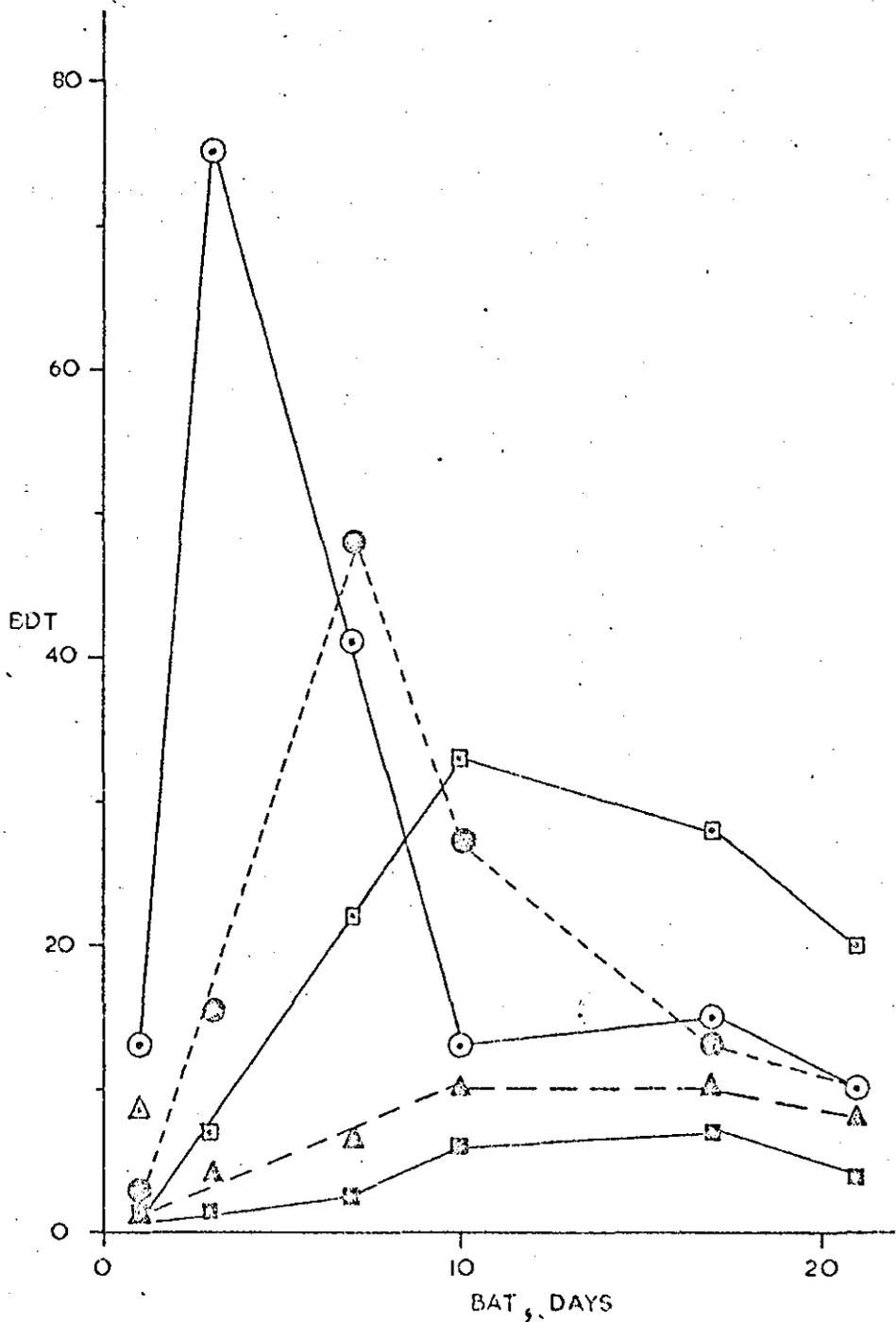


Figure 3.5 Effect of Aerosil 300 concentration in E302 on the relationship between breakdown time (BDT) and bin-ageing time (BAT) at room temperature  
 (○ 48 phr      △ 40 phr crepe-hardened  
 ⊙ 32 phr    □ 24 phr    △ 16 phr    □ 8 phr)

Table 3.3 Effect of fillers and bin-ageing time at 70°C on breakdown time, min

Filler	Aerosil 300	Aerosil 200	EP 154	Celite Superfloss
Bin-ageing time at 70°C				
1 day	80	40	1	$\frac{1}{4}$
2 days	53	39	2½	$\frac{1}{4}$
3 days	42	32	7½	$\frac{1}{4}$
4 days	24	28	12	$\frac{1}{4}$

E303 containing 32 phr of filler, as stated

### 3.6 EFFECT OF ADDITIVES

Addition of only 0.1 phr of morpholine at the end of a mixing cycle had a very pronounced effect on processibility: E303 containing 32 phr of Aerosil 300 crumbled almost instantaneously, while with only 8 phr of Aerosil 300 very considerable increase in breakdown time was recorded. With 32 phr of EP 154 0.1 phr of morpholine again produced a considerable increase in breakdown time but there was no detectable change with Celite Superfloss: values obtained after bin-ageing for one day are summarised in Table 3.4. Following bin-ageing in morpholine vapour for 2 weeks a small portion of the mix with 32 phr of Aerosil 300 was found to be processible; later a breakdown time of  $3\frac{1}{2}$  minutes was obtained.

E303 containing 32 phr of Aerosil 300 and bin-aged for 2 days at 70°C had a breakdown time of 74 minutes in comparison with a breakdown time of 76 minutes for a mix which only differed in the addition of 0.1 phr of DPPH before addition of the filler.

The very large difference in effectiveness of these two additives i.e. morpholine - a strong catalyst for siloxane bond reactions and DPPH - a free radical acceptor, provides strong but not conclusive evidence that the interaction between E303 and Aerosil 300 is due to a chemical reaction involving siloxane bonds.

Table 3.4 Effect of morpholine and filler on the  
breakdown time of E303

Filler	Filler concentration, phr	Morpholine concentration, phr	Breakdown time, min
Aerosil 300	32	0.1	unprocessible
	8	0.1	12
	8	nil	$\frac{1}{4}$
EP 154	32	0.1	30 (rough)
	32	nil	1
Celite Superfloss	32	1.0	$\frac{1}{4}$
		nil	$\frac{1}{4}$

Mixes bin-aged for 1 day

### 3.7 CONCLUSIONS

The increase in breakdown time on bin-ageing silicone rubber containing Aerosil 300 is indicative of some considerable interaction, probably between the polymer and filler: at least part of the effect could be due to filler-filler interaction.

As in other published work there is contradictory evidence concerning the nature of the interaction, with the activation energy of the decrease in processibility indicating a physical reaction but the effect with morpholine indicating a chemical reaction. One possible explanation is that the interaction between polymer and filler is chemical but that its rate is determined by the diffusion of the polymer to the filler: an explanation which is enhanced by the higher rate of reaction of lower molecular weight polymer (Figure 3.3).

The decrease in breakdown time on successive determinations illustrates the thixotropy of these mixes because the breakdown time of a mix immediately after a determination is virtually zero. Usually there is not full recovery of the original structure within a week thus indicating that filler-filler interactions are not wholly responsible for the thixotropy. The occasional increase in breakdown time between successive determinations is probably due to further breakdown of filler aggregates during a determination, and thus greater exposure of reactive sites on the filler surface.

The dependence on active sites is also shown by the low values of breakdown time observed with surface treated Aerosil 300 (i.e. EP 154) and with coarser fillers such as Celite Superfloss.

The eventual decrease in breakdown time of mixes not previously remilled is further evidence of some interaction other than any between filler particles. It is proposed that adsorbed rubber and interparticular rubber are mainly responsible for the observed effects, with the latter reducing the processibility.

It must be remembered that the breakdown time determination involves milling of the mix and thus alteration of the molecular structure, particularly mechanical scission of interparticular rubber. As long as many of the active sites on the filler surface remain, broken interparticular rubber can reform: in the extreme the concentration of interparticular rubber can actually increase during milling and thus crepe-harden. If broken interparticular rubber cannot reform as interparticular rubber it remains as adsorbed rubber to supplement any formed directly: thus adsorbed rubber increases on bin-ageing and, even more so, on remilling. On successive bin-ageing and remilling cycles, therefore, adsorbed rubber becomes the favoured structure and, finally, Aerosil 300 behaves like EP 154.

## CHAPTER 4 IMMERSION IN ORGANIC LIQUIDS

### 4.1 BOUND RUBBER IN TOLUENE

#### 4.1.1 Effect of immersion time (unvulcanised mixes)

The bound rubber values recorded in Table 4.1 confirmed that, with E302 and irrespective of Aerosil 300 concentration, equilibrium was not positively established during immersion for 14 days; indeed after 30 days bin-ageing they were still decreasing at a rate proportional to the square root of immersion time: nevertheless at any given filler concentration and immersion time bound rubber increased during bin-ageing.

An increase to 8 separate determinations, with a maximum of 100 days immersion of portions bin-aged for 71 days, still failed to establish equilibrium bound rubber; again bound rubber decreased at a rate proportional to the square root of the immersion time after the first 4 days (Figure 4.1). However it was discovered that the intercepts, of the extrapolated linear regions, at zero immersion time, were linearly related to the logarithm of the filler concentration (Figure 4.2).

Using the alternative technique of continuing immersion until three successive weekly determinations of solution concentration had revealed the absence of sol rubber it was found possible to obtain equilibrium values of bound rubber

Table 4.1 Bound rubber of E302 containing various concentrations of Aerosil 300

Filler concentration, phr		8	16	24	32	40	48
Bin-ageing time, days	Immersion time, days						
1	1	NP	NP	NP	38.4	55.9	53.1
	2	NP	NP	NP	27.8	45.8	49.4
	7	NP	NP	NP	25.0	39.3	46.1
	14	NP	NP	NP	23.7	39.9	44.9
7	1	NP	69.5	75.3	83.0	86.6	85.2
	2	NP	51.5	55.0	72.3	81.1	80.3
	7	NP	27.2	35.2	51.7	72.5	72.3
	14	NP	19.5	27.1	40.2	65.4	66.7
14	1	NP	79.9	84.4	83.3	88.5	87.0
	2	NP	58.5	65.6	78.3	85.0	86.3
	7	NP	34.4	39.8	59.2	74.6	78.8
	14	NP	26.4	29.3	43.6	61.4	71.6
30	1	NP	76.0	82.5	91.0	92.2	89.9
	2	NP	59.5	74.5	82.3	85.9	88.3
	7	NP	40.8	55.2	66.0	81.0	81.5
	14	NP	29.1	37.7	43.6	74.5	75.8

NP Gel too weak to handle

Separate test-piece used for each determination

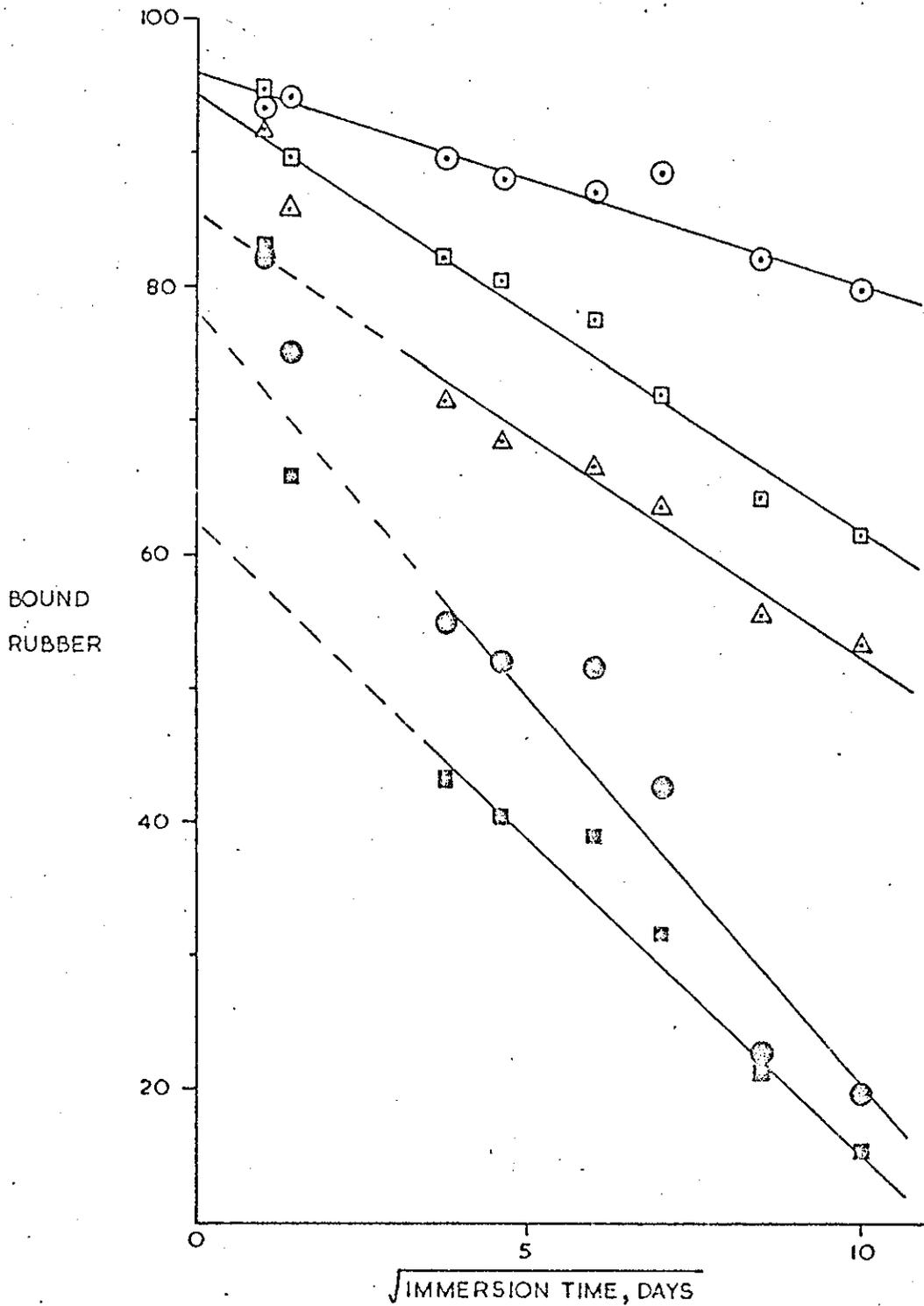


Figure 4.1 Dependence of bound rubber on the square root of immersion time for E302 containing Aerosil 300  
 (○ 48 phr □ 32 phr △ 24 phr  
 ⊙ 16 phr ⊠ 8 phr)

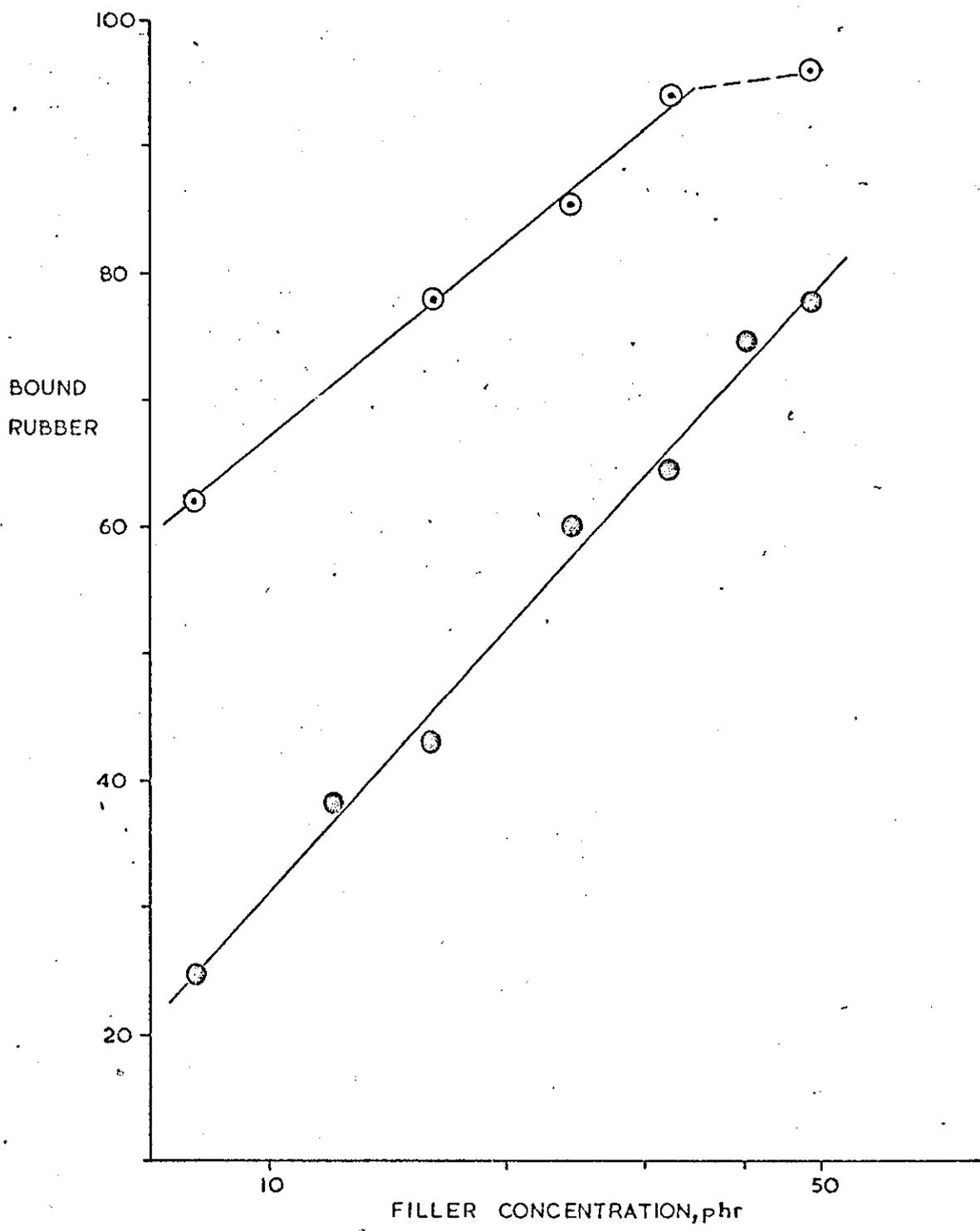


Figure 4.2 Relationship between filler concentration and bound rubber for Aerosil 300 in E302 ( ○ extrapolated zero time values from Figure 4.1 ● equilibrium values, after bin-ageing alone for 84 days, from Table 4.2)

The values, given in Table 4.2, established that bound rubber, whether after 1 day immersion or at equilibrium, increased with increase of filler concentration, on heat treatment and on bin-ageing: again values were proportional to the logarithm of filler concentration (Figure 4.2). The immersion times necessary to establish equilibrium conditions ranged from 9 to 32 weeks (Table 4.3).

Continuous immersion of test-pieces of E302 containing 26 phr of Aerosil 300 subsequently revealed that, in some cases, sol rubber could be extracted almost indefinitely (Figure 4.3) and showed that the previous criterion of no detectable sol in three weeks could have been inadequate.

A better criterion for establishing that bound rubber had attained a true equilibrium value on immersion would have been to require a plot of bound rubber against the square root of immersion time to show a definite change to zero slope, as had been shown previously for certain mixes which required less than 1 month immersion (Southwart 1969 2). It will be shown later that a normal determination of the bound rubber of a test-piece containing Aerosil 300 has a permanent effect on subsequent behaviour in a liquid, thus precluding a simple method of successive determinations on one sample until equilibrium is definitely established.

Even when a true equilibrium value of bound rubber was determined there remained the possibility that there had been a higher true value when the test-piece was first immersed and that some of that bound rubber had been solubilised during the immersion. To eliminate polymer-filler interaction

Table 4.2 Effect of filler concentration, bin-ageing time and mix treatment on bound rubber (E302)

Bin-ageing time, days	Mix treatment	Immersion condition*	Concentration of Aerosil 300, phr						
			8	12	16	24	32	40	48
0	mixed only	1 day	11.9 <sup>†</sup>	8.8	6.4	9.8	17.5	20.0	35.0
		equilibrium	0	2.3	0	1.0	2.2	12.2	17.4
	heated	1 day	33.8	43.4	53.6	72.0	82.9	76.0	83.5
		equilibrium	29.9	37.6	46.5	63.8	76.7	81.7	81.4
	heated and remilled	1 day	88.5 <sup>†</sup>	68.9	64.3	83.5	86.5	80.5	83.6
		equilibrium	too weak	23.8	44.0	52.5	57.8	66.8	59.6
84	mixed only	1 day	45.4	48.2	58.1	88.5	91.5	87.0	93.0
		equilibrium	24.7	38.3	43.0	60.0	64.6	74.8	77.8
	heated	1 day	39.5	50.8	57.8	79.5	92.1	82.5	94.0
		equilibrium	32.7	43.6	53.5	69.3	74.3	76.3	92.8
	heated and remilled	1 day	70.0	74.5	76.9	91.6	93.0	93.9	95.0
		equilibrium	32.6	42.4	51.6	70.0	77.7	77.6	86.0

\* Immersion conditions  
 1 day: single test-pieces  
 equilibrium: four test-pieces (median value quoted)  
 heat treatment 4 hours at 250°C

<sup>†</sup> solution method

Table 4.3 Immersion time, weeks required to establish equilibrium bound rubber (Table 4.2)

Bin-ageing time, days	Mix treatment	Concentration of Aerosil 300, phr						
		8	12	16	24	32	40	48
0	mixed only	14	14	14	14	28	14	28
	heated	9	9	9	9	10	9	10
	heated and remilled	-	32	32	32	28	32	28
84	mixed only	17	17	17	17	22	17	22
	heated	13	13	13	13	22	13	22
	heated and remilled	17	17	17	17	25	17	25

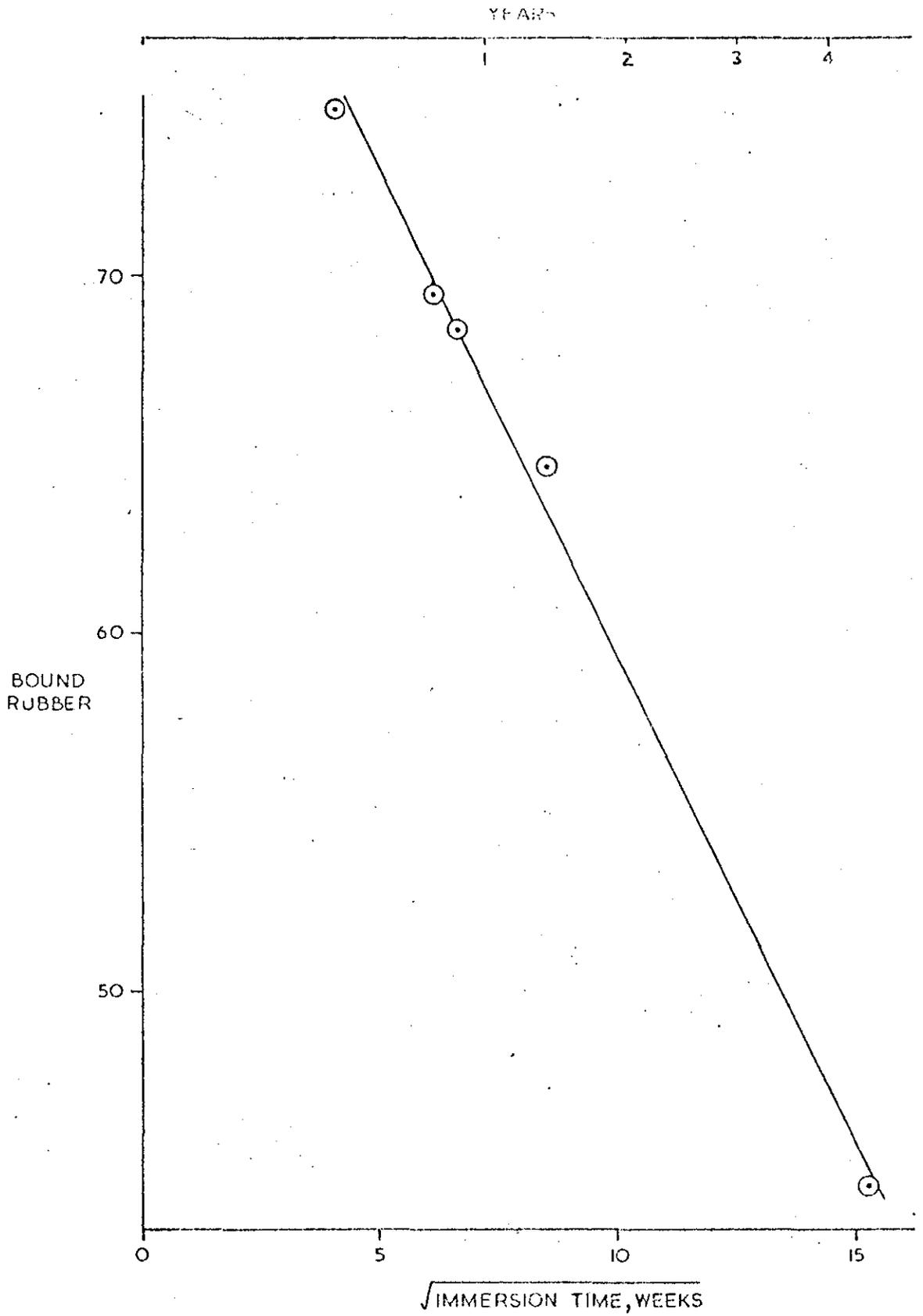


Figure 4.3 Dependence of bound rubber on the square root of immersion time in toluene for E302 containing 26 phr of Aerosil 300

from further investigation of the effect of immersion time lightly crosslinked unfilled silicone rubber was adopted as a model system.

#### 4.1.2 Effect of immersion time (gum vulcanisates)

Successive determinations of "bound rubber" on two lightly crosslinked portions of E303 revealed (Figure 4.4) that, even in the absence of filler, nearly 7 days immersion was required to extract 9% soluble rubber while at least 27 days immersion was required to extract nearly 30% soluble rubber.

When the swollen extracted gel was subsequently immersed in a solution of E303 the rate of absorption of polymer was found to be even slower than had been the rate of desorption.

Although the rates of extraction were higher in the absence of silica the general dependence on square root of immersion time indicates that the difficulty in achieving an equilibrium value of bound rubber in the presence of silica is due mainly to the diffusion behaviour of the soluble silicone rubber and not to the occurrence of solubilising reactions: differences in rate of extraction were presumably due to differences in the swelling of the gel (Section 4.8).

#### 4.1.3 Effect of bin-ageing

A rapid increase in bound rubber on bin-ageing was shown by the values in Table 4.1, particularly those after immersion for only 1 day. Previous results indicated that

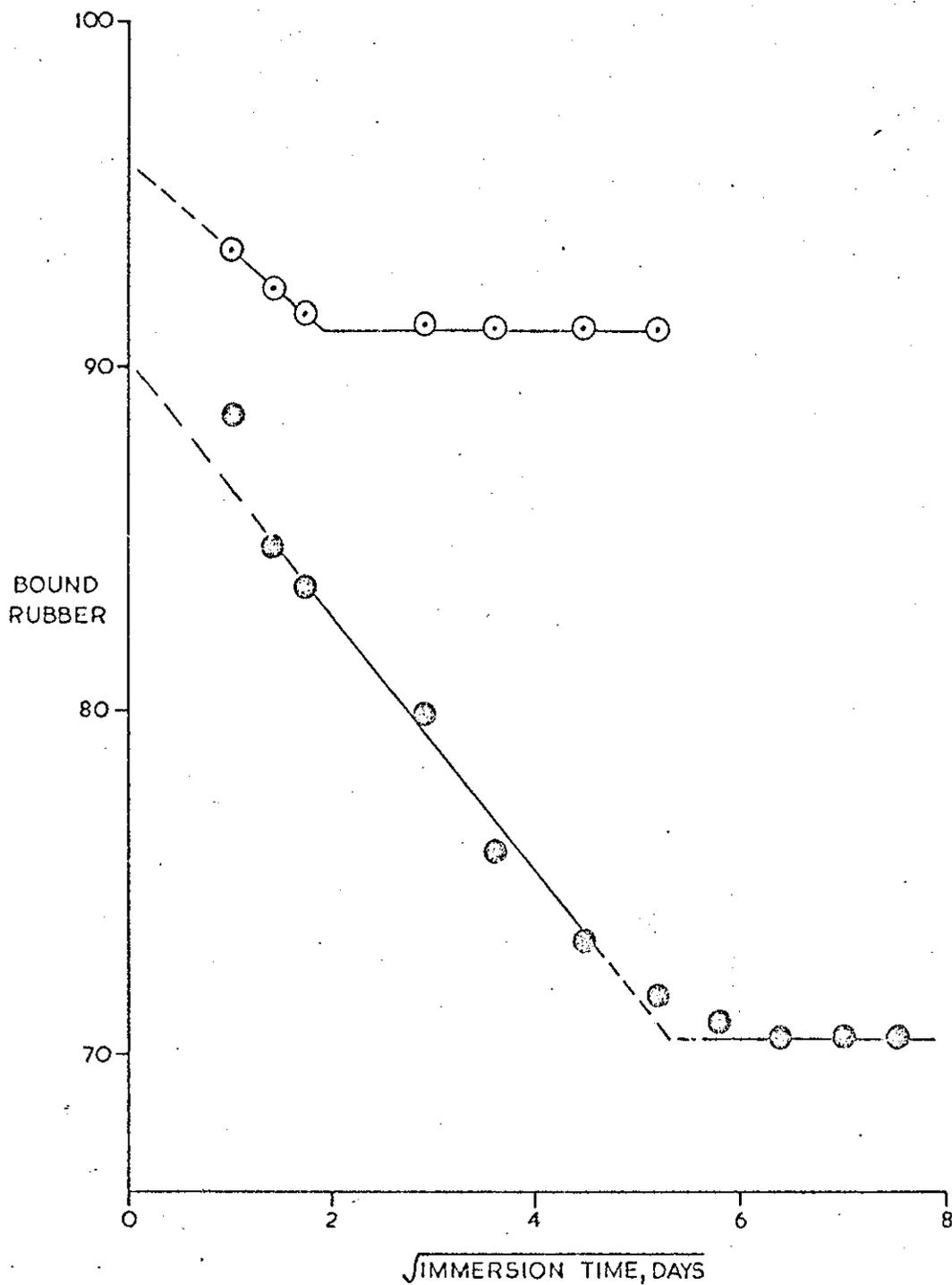


Figure 4.4 Dependence of "bound rubber" on the square root of immersion time for E303 gum vulcanisates (mean of duplicated values) (Peroxide concentration  $\odot$  0.5 phr  $\ominus$  0.2 phr)

the increase in bound rubber was proportional to the square root of bin-ageing time but with a change in slope after a few days (Southwart 1969 2).

Bound rubber of E303 containing 32 phr of Aerosil 300 was determined after various bin-ageing times including very low ones, and 1 day immersion (Table 4.4). With such low times it was necessary to allow for some interaction occurring as soon as some of the filler had been added to the rubber and half the 30 min mixing time seemed appropriate: the bound rubber confirmed the previous relationship when plotted against the square root of the adjusted bin-ageing time (Figure 4.5).

Similar allowance was made in a duplicate experiment except that the mix was divided immediately after mixing for bin-ageing at room temperature and at 8°C. At both temperatures bound rubber was proportional to the square root of the adjusted bin-ageing time (Figure 4.6) and in good agreement with the previous zero time value. The rate of increase of bound rubber was temperature dependent and the difference indicated an activation energy of approximately 0.03 MJ/mol in good agreement with the values of Wagner and Sellers (Section 1.3) and thus implying chemisorption of the rubber.

Morpholine had a very significant effect on bound rubber (1 day immersion). In E303 containing 8 phr of Aerosil 300 0.1 phr immediately increased the bound rubber to the range 65-70 compared with the immediate 16, and the final 62 obtained after 10-14 days, in its absence. This also indicated chemical reaction between polymer and filler.

Table 4.4 Bound rubber of E303 containing  
32 phr of Aerosil 300 determined  
after immersion for 1 day

Bin-ageing time, hours	Bound rubber
0	17.6
0.5	21.4
1	26.6
2	29.5
4	35.4
6	46.1
24	75.2
48	82.9
72	88.9
168	89.5

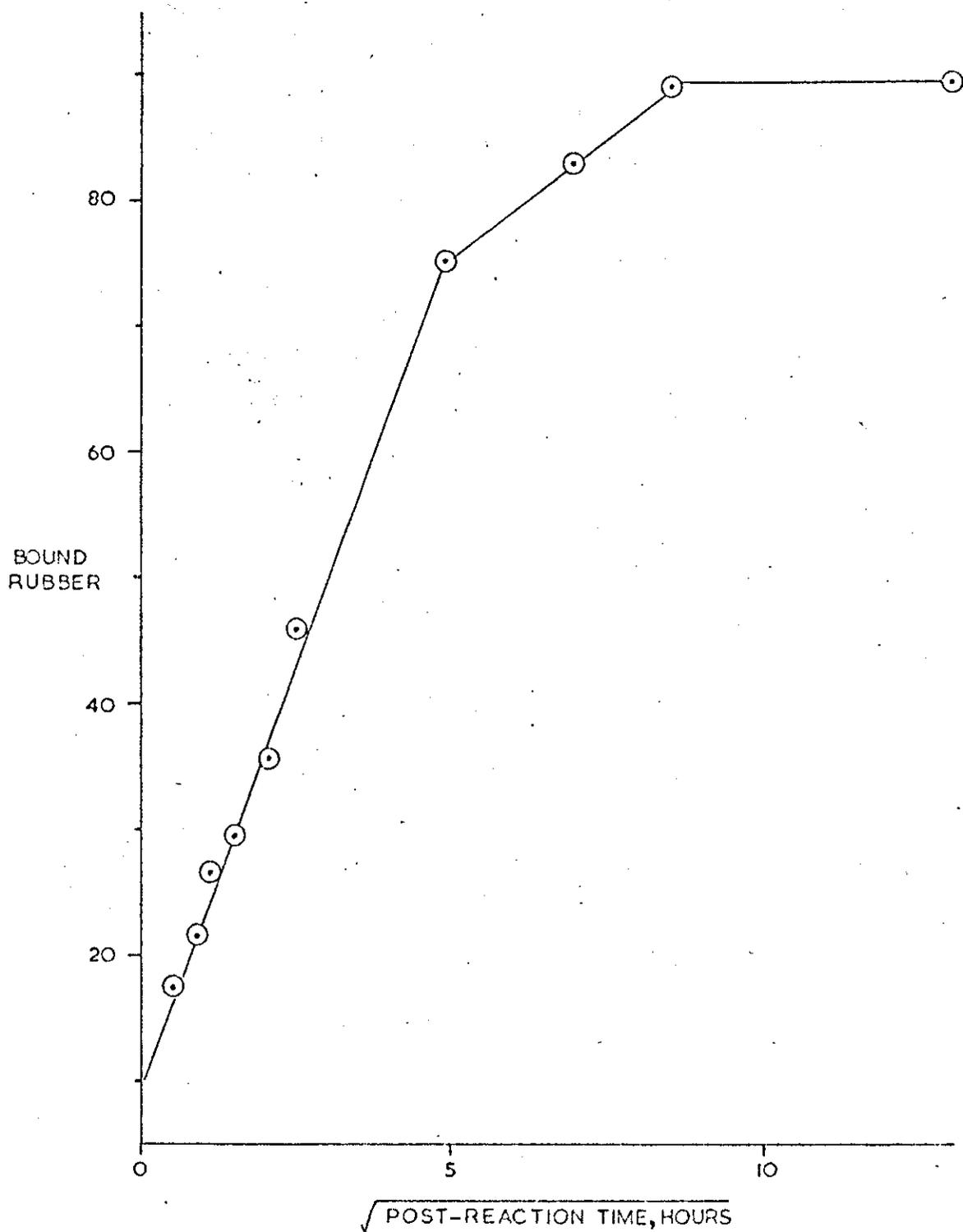


Figure 4.5 Dependence of bound rubber on the square root of bin-ageing time for E303 containing 32 phr of Aerosil 300, after allowance for interaction occurring during mixing

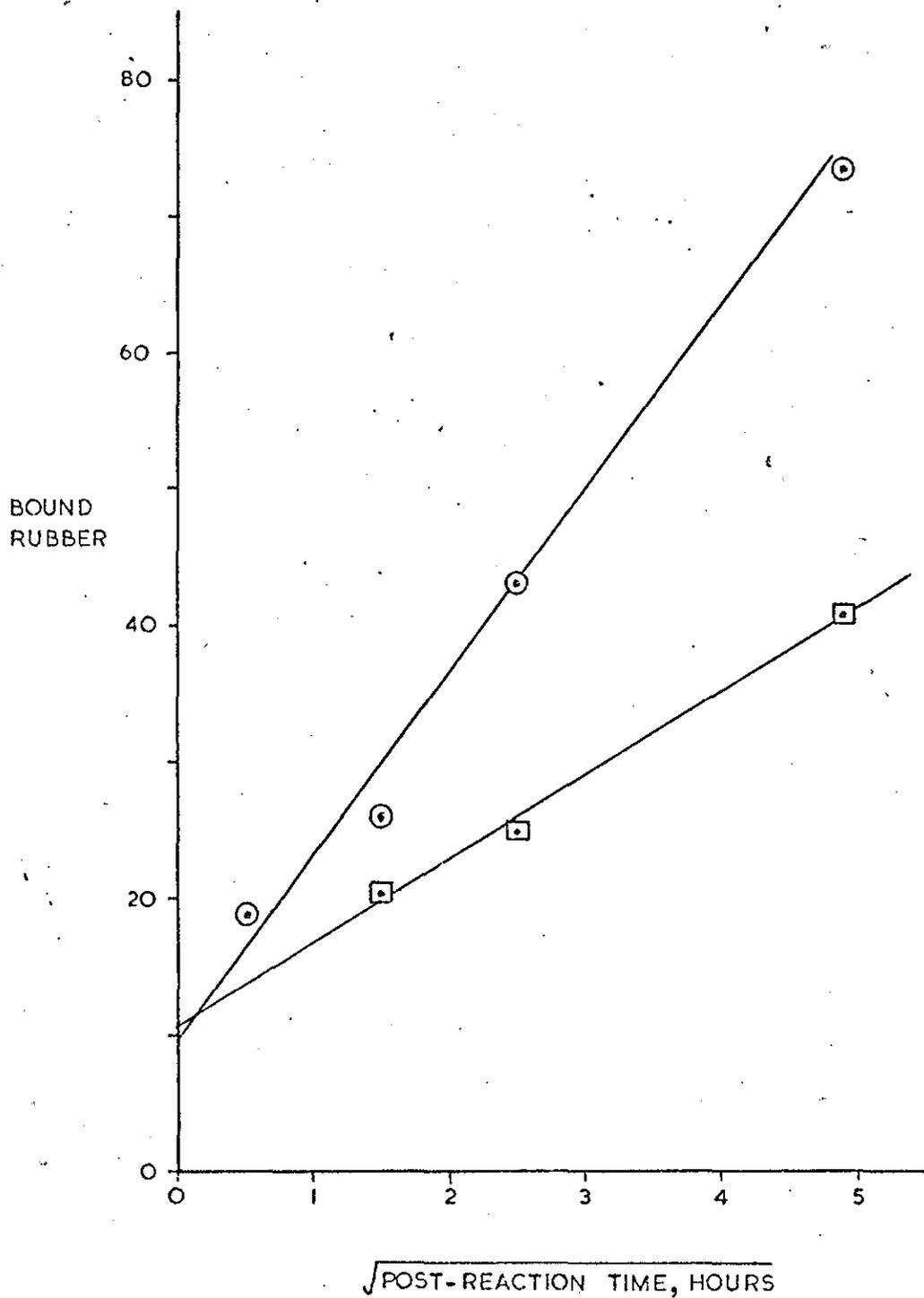


Figure 4.6 As Figure 4.5  
 (Bin-ageing temperature,  
 ○ 21°C □ 8°C)

The bin-ageing in morpholine vapour of the E303 mix with 32 phr of Aerosil 300, rendered unprocessable by the presence of 0.1 phr of morpholine, eventually reduced the bound rubber (24 hour immersion) to only 30, implying chemical reaction of a different type e.g. hydrolysis.

#### 4.1.4 Effect of filler type and concentration

The values in Tables 4.1 and 4.2 confirmed the increase in bound rubber with increase in concentration of Aerosil 300.

Typical values illustrative of the increase in bound rubber (1 day immersion) with increase in specific surface area of untreated silica, and the lower reactivity of treated silica are given in Table 4.5.

The very low reactivity of Celite Superfloss (32 phr in E303) was also shown by the absence of bound rubber even in the presence of 1 phr of morpholine.

Several fillers were further compared in E302 by determination of bound rubber after heat treating the mixes to simulate the thermal effects of vulcanisation (Table 4.6).

#### 4.1.5 Osmotic pressure effect

Blow (1973) showed that improved linearity was obtained when the author's previous results (Southwart 1969 2) of bound rubber of gels immersed in rubber solutions were

Table 4.5 Dependence of bound rubber (1 day immersion) on filler type and bin-ageing time

Filler*	Bin-ageing time, days		
	0	2	7
EP 154	3	50	66
Aerosil 300	43	85	92
Aerosil 200	27	83	91
Celite Superfloss	Nil	Nil	Nil

\* 32 phr in E303

Table 4.6 Effect of heating on the bound rubber of E302 containing various fillers

Filler	Filler concentration, phr	Treatment temperature, °C	Bound rubber
SAF black	75	171	16
MT black	200	150	12
Minusil	200	170	16
Celite Superfloss 120		110	13

plotted against  $S'_s T_2/T_3$  (Section 11.4) rather than against solution concentration. Nevertheless there was little effect on the intercept value which was designated "true" bound rubber but which was really bound rubber in pure solvent i.e. the value of bound rubber in the absence of any osmotic pressure or back pressure effect. Blow also found that the "true" bound rubber was almost directly proportional to the partition coefficient (P) i.e. the slope of the original plot (Section 11.4).

If the partition coefficient is proportional to the equilibrium bound rubber, and independent of immersion time, a limited period of immersion in two or more polymer solutions of different concentrations would enable the equilibrium bound rubber to be determined from the partition coefficient once the relationship had been established.

Bound rubber determined on previously unextracted portions of a gum vulcanisate, chosen to avoid filler effects, after different periods of immersion, was plotted against  $S'_s T_2/T_3$  (Figure 4.7) and the values of partition coefficient calculated from the slopes of the lines as drawn are given in Table 4.7. Bound rubber (pure toluene) decreased as immersion time was increased but surprisingly it did not reach the equilibrium value of  $91.1 \pm 0.1$ , separately determined, within 3 weeks. Partition coefficient was not constant but the mean value was very close to the 0.080 obtained apparently irrespective of immersion time, with extracted test-pieces (Figure 4.8),

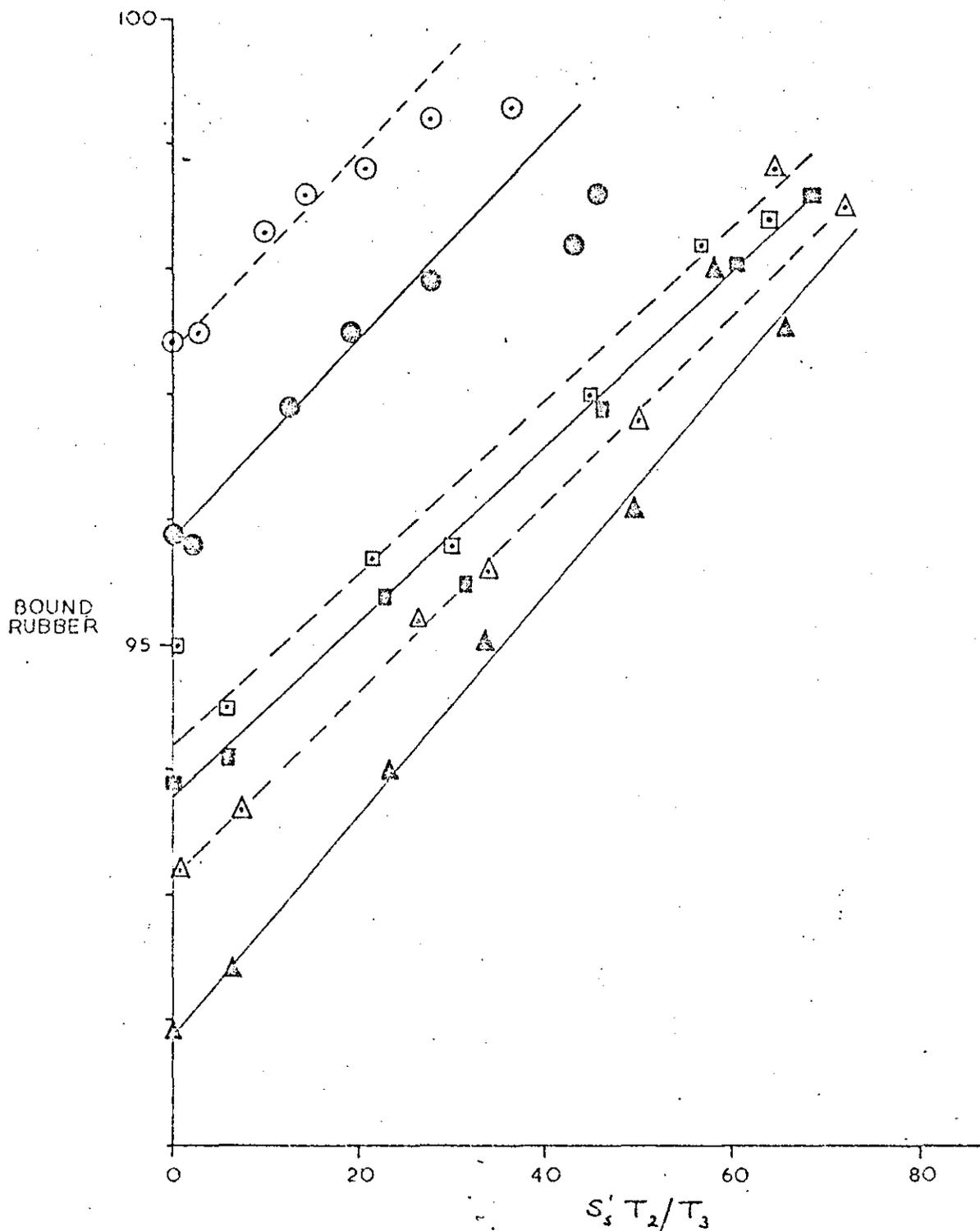


Figure 4.7 Osmotic pressure effect (Section 11.4) for an E303 vulcanisate (0.5 phr of peroxide) immersed for various total times, hours (⊙ 2 ⊗ 6 □ 24 ▣ 48 △ 96 ▲ 504)

Table 4.7 Partition coefficient and "true" bound rubber of E303 vulcanisates

Immersion time	Partition coefficient	"True" bound rubber
<u>0.5 phr peroxide</u>		
2 hours	0.075	97.4
6 hours	0.079	95.9
1 day	0.069	94.2
2 days	0.070	93.8
4 days	0.074	93.1
3 weeks	<u>0.088</u>	91.8
	mean <u>0.076</u>	
<u>0.2 phr peroxide</u>		
6 weeks	0.27	70.0
6 weeks	0.23	71.0

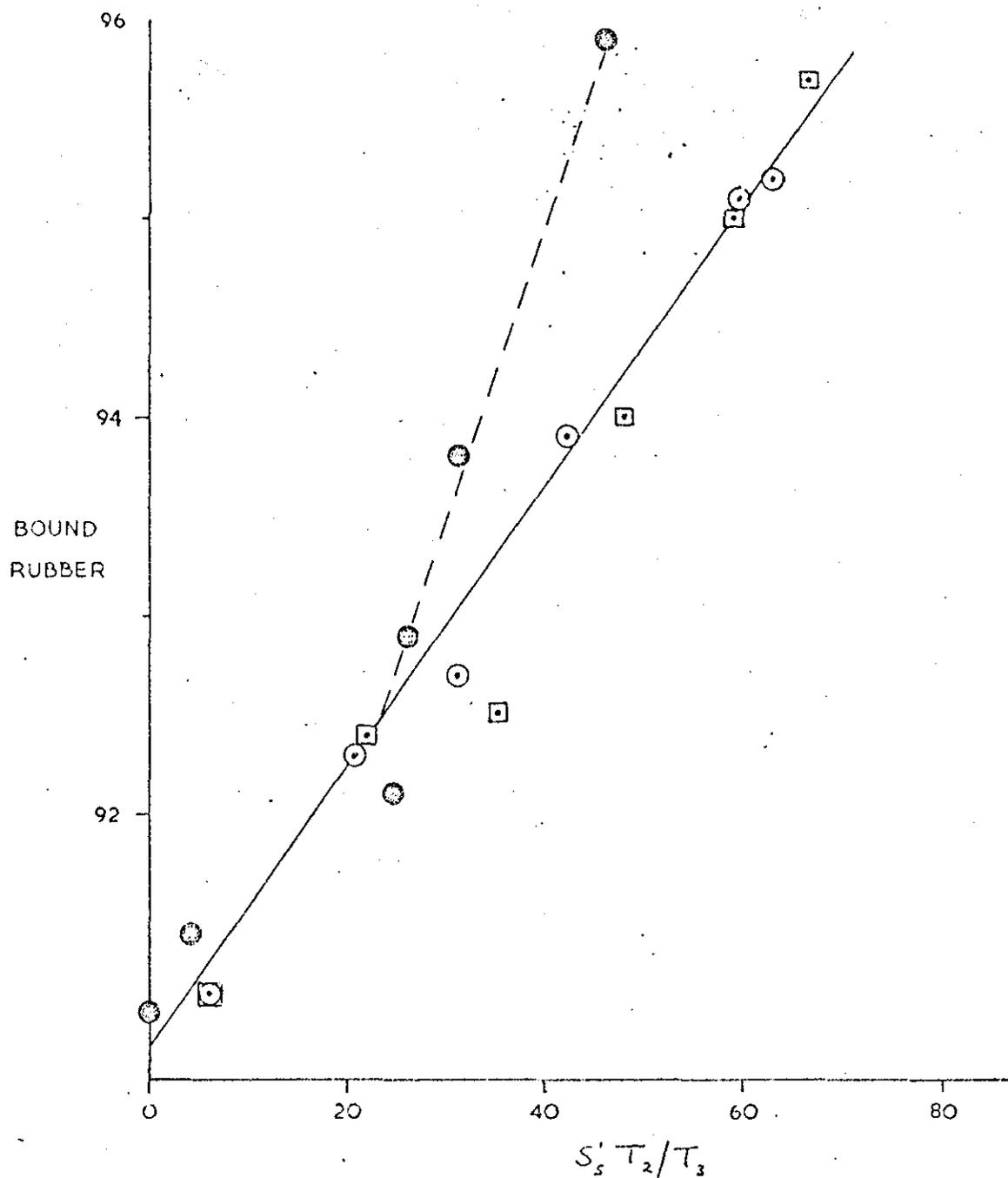


Figure 4.8 As Figure 4.7 but test-pieces previously extracted

(Total immersion time, hours ● 4    ⊙ 24  
 □ 48)

except that some deviation was recorded after immersion for only 4 hours.

Partition coefficient (Table 4.7) was also calculated on duplicate test-pieces of the lightly crosslinked E303 vulcanisate (Section 4.1.2).

With filled mixes the results were more complex due to the additional effects of bin-ageing: values obtained with E303 and 32 phr of Aerosil 300, after bin-ageing for 0, 1 and 4 days, are given in Figure 4.9. The solid symbols and lines were obtained with unextracted test-pieces and reveal decreasing partition coefficient with increasing bound rubber: the open symbols and dashed lines were obtained with test-pieces extracted to substantially equilibrium bound rubber before immersion in polymer solutions and reveal little difference in partition coefficient after 1 day's bin-ageing. Partition coefficients calculated from the lines as drawn are given in Table 4.8, together with the values of bound rubber (pure solvent).

To test the relationship between bound rubber and partition coefficient the values were plotted in Figure 4.10, with open symbols for extracted test-pieces and/or use of equilibrium bound rubber, and half open symbols for the test-pieces in the earlier work as the values quoted by Blow (1973) were independent of extraction.

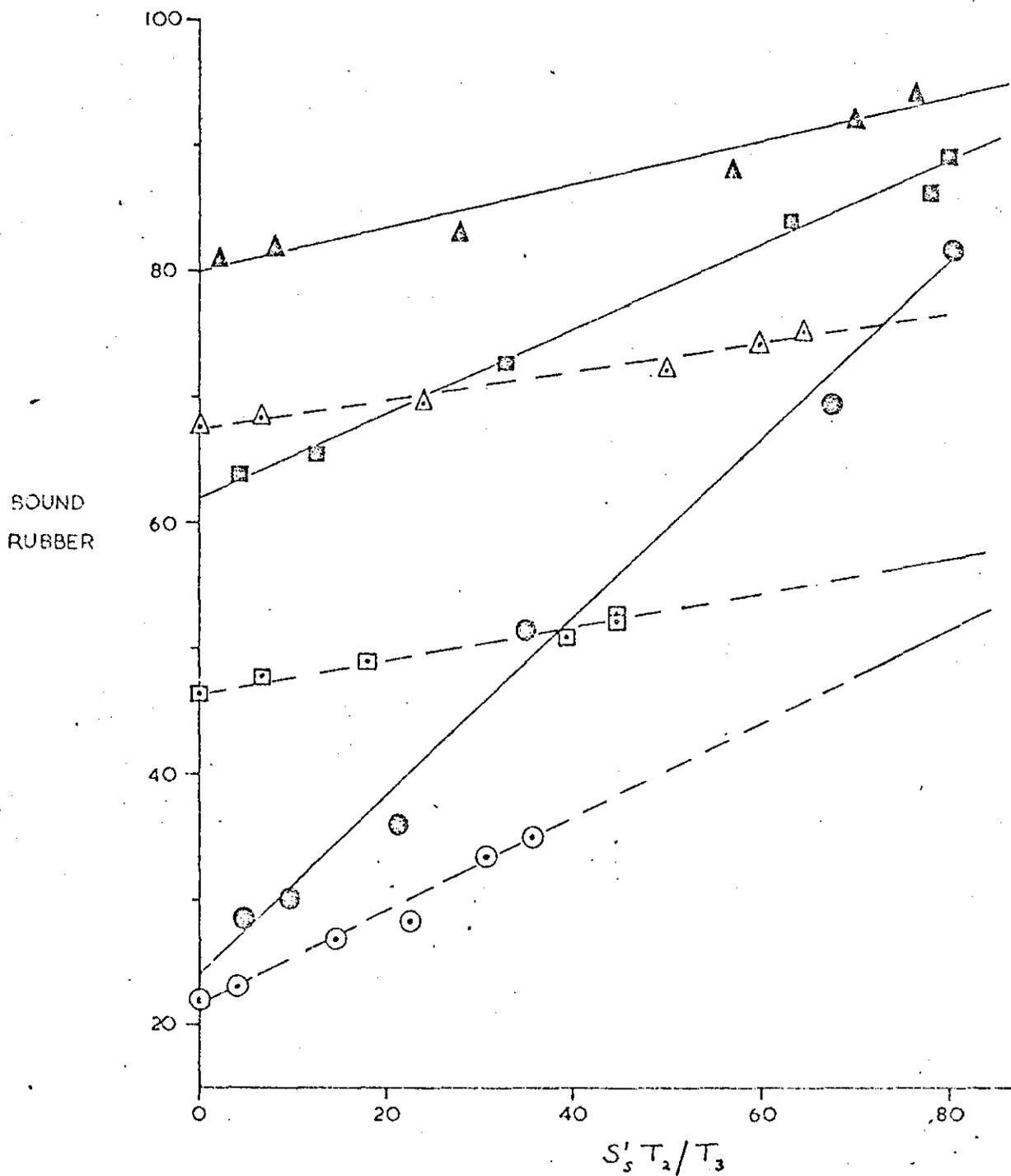


Figure 4.9 Osmotic pressure effect (Section 11.4) for E303 containing 32 phr of Aerosil 300 bin-aged for 0 days  $\odot \ominus$ , 1 day  $\square \blacksquare$  and 4 days  $\triangle \blacktriangle$  (open symbols - extracted test-pieces)

Table 4.8 Partition coefficient and bound rubber  
calculated from Figure 4.9

Bin-ageing time, days	Unextracted	Extracted
	<u>Partition coefficient</u>	
0	0.71	0.37
1	0.33	0.13
4	0.17	0.11
	Non-equilibrium bound rubber	Equilibrium bound rubber
0	24	22
1	62	46.5
4	80	67.5

Legend for presentation of above data in Figure 4.10

Test-pieces	Unextracted	Unextracted	Extracted
Bound rubber	Non-equilibrium	Equilibrium	Equilibrium
Symbol	■	□	△

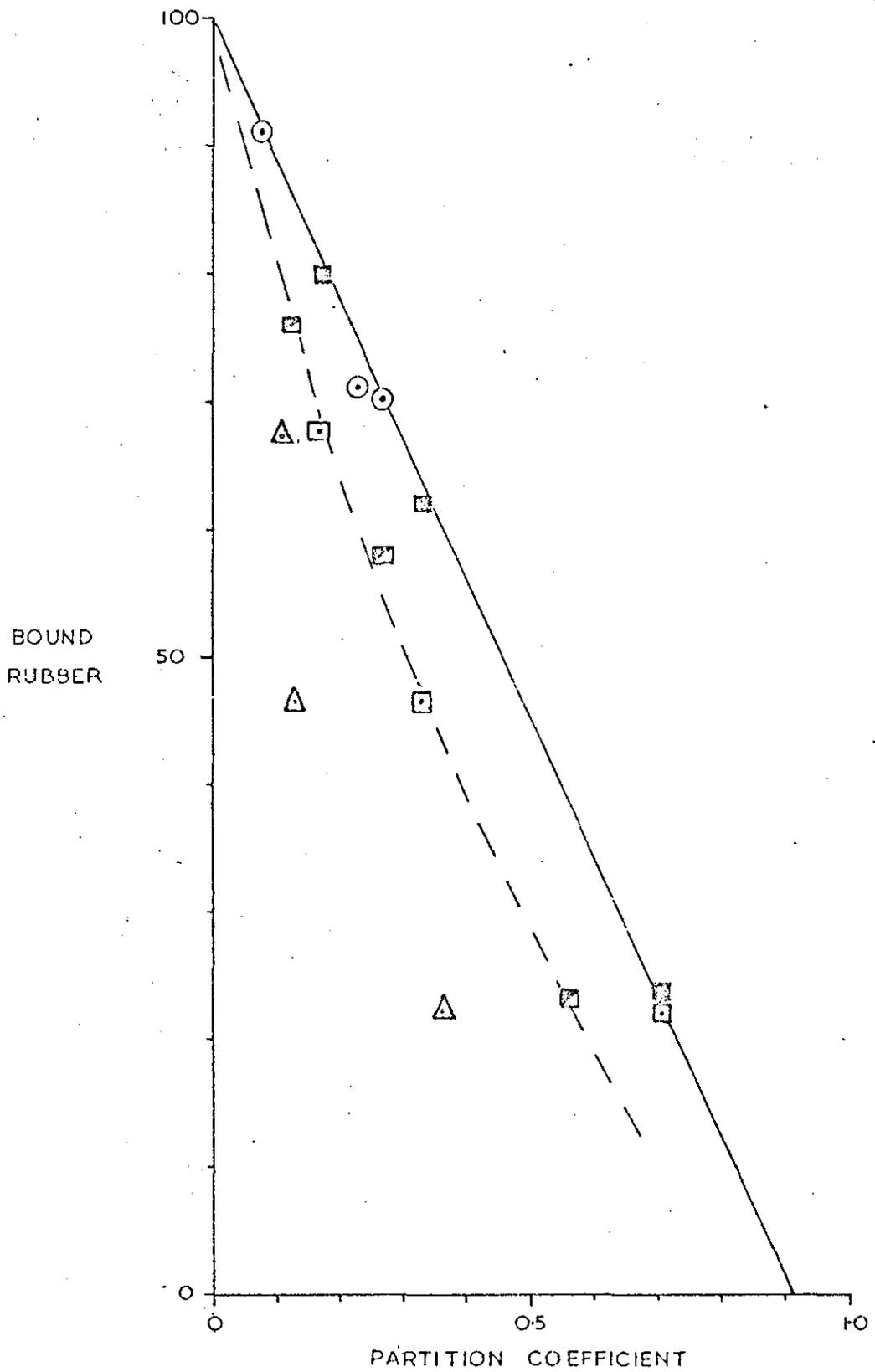


Figure 4.10 Relationship between bound rubber and partition coefficient using data from Table 4.7  $\odot$ , Table 4.8  $\square$   $\blacksquare$   $\triangle$  and Blow 1973 Table 6  $\boxtimes$ .

The data provide considerable support for the theory of a relationship between bound rubber and partition coefficient, with the solid line for unfilled vulcanisates and the dashed line for filled unvulcanised mixes. The two sets of deviations from the dashed line are interesting. The (non-equilibrium) values for unextracted test-pieces fall on the solid line while the (equilibrium) values for extracted test-pieces appear in isolation.

It is possible that some changes were occurring in the network during the immersion and that the relationship is only valid under certain conditions of bin-ageing and immersion. If these limitations can be established partition coefficient may yet prove a valuable tool for the analysis of bound rubber.

## 4.2 BOUND RUBBER IN OTHER LIQUIDS

### 4.2.1 Gum vulcanisates

Bound rubber of the E303 vulcanisate (0.5 phr of peroxide) was determined successively on portions immersed in various liquids and plotted against the square root of immersion time (Figure 4.11) to reveal that the equilibrium value, and rate of decrease, of bound rubber were dependent on the liquid, and that the time to equilibrium was not a simple function of the amount of rubber extracted. Subsequent immersion of all the samples in hexane gave equilibrium values of  $90.6 \pm 0.1$

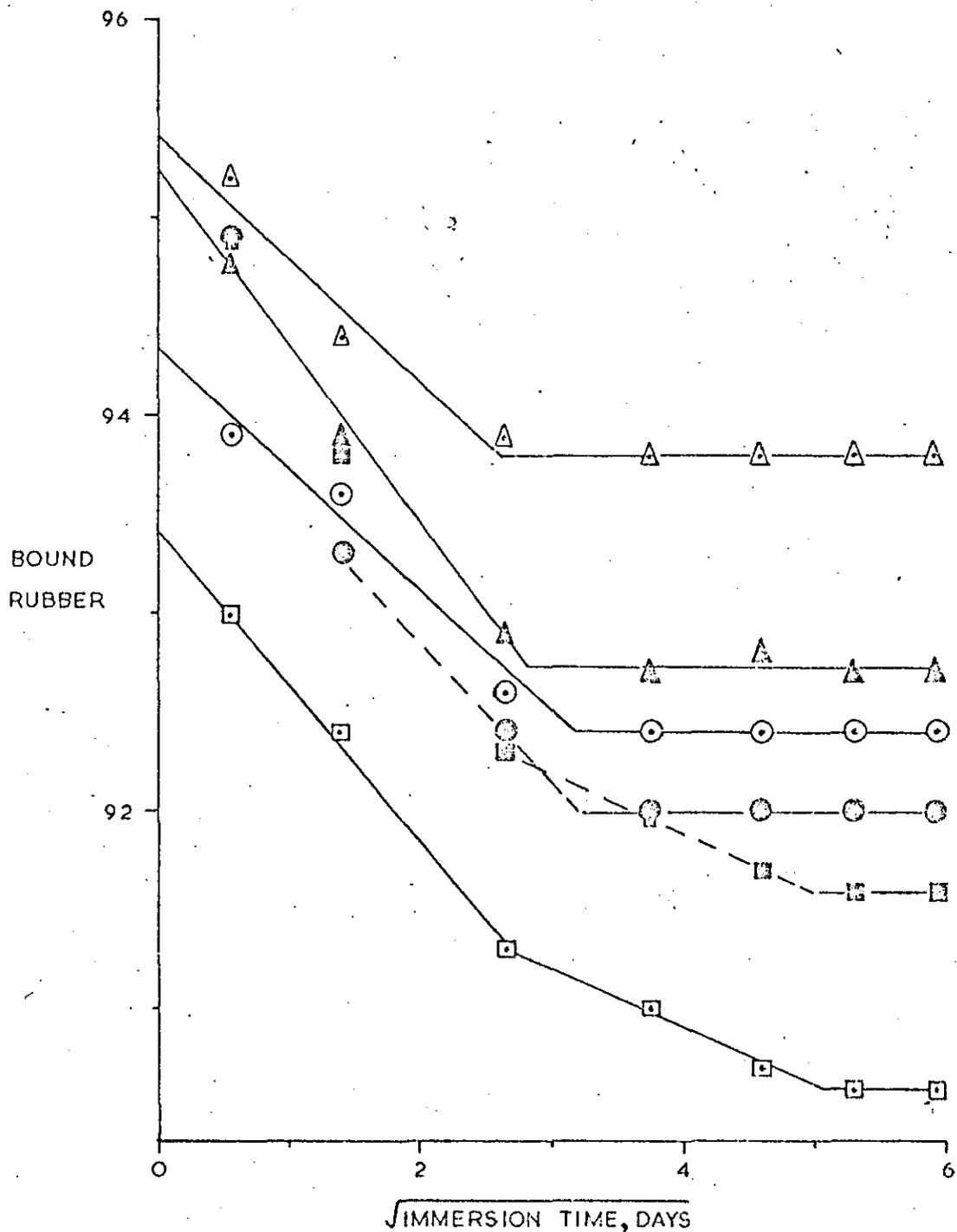


Figure 4.11 Dependence of "bound rubber" on the square root of immersion time for an E303 vulcanisate (0.5 phr of peroxide) in various liquids  
 (Δ acetone    ○ toluene    ◻ hexane  
 ▲ methyl isobutyl ketone  
 ⊙ methyl ethyl ketone. ◻ tetrahydrofuran)

and thus confirmed that there had been no significant change within the samples to account for the liquid dependent (first) equilibrium.

Similar values obtained following continuous immersion for seven weeks (with several transfers to fresh liquid) confirmed that successive drying down and reswelling had no effect on the final values from a gum vulcanisate.

Similarly the equilibrium bound rubber of the other E303 vulcanisate (0.2 phr of peroxide) was shown to be much higher in acetone than in hexane but the intermediate values plotted against the square root of immersion time lay on fairly smooth curves rather than on straight lines. The dependence of equilibrium bound rubber on liquid is shown later to be related to the molecular weight of the extracted rubber (Section 4.5).

#### 4.2.2 Filled mix

Bound rubber of E303 containing 32 phr of Aerosil 300 (bin-aged 3 weeks at 8°C) obtained successively on duplicate portions immersed in various liquids was plotted against the square root of immersion time (Figure 4.12). As with the gum vulcanisate the equilibrium value was dependent on the liquid. Quite differently from the gum vulcanisate, however, there was no further extraction of polymer on transfer to hexane with the exception of 2% from the acetone extracted portion: this confirmed that there was some further adsorption of polymer on filler during the determination, most likely while the liquid concentration was low.

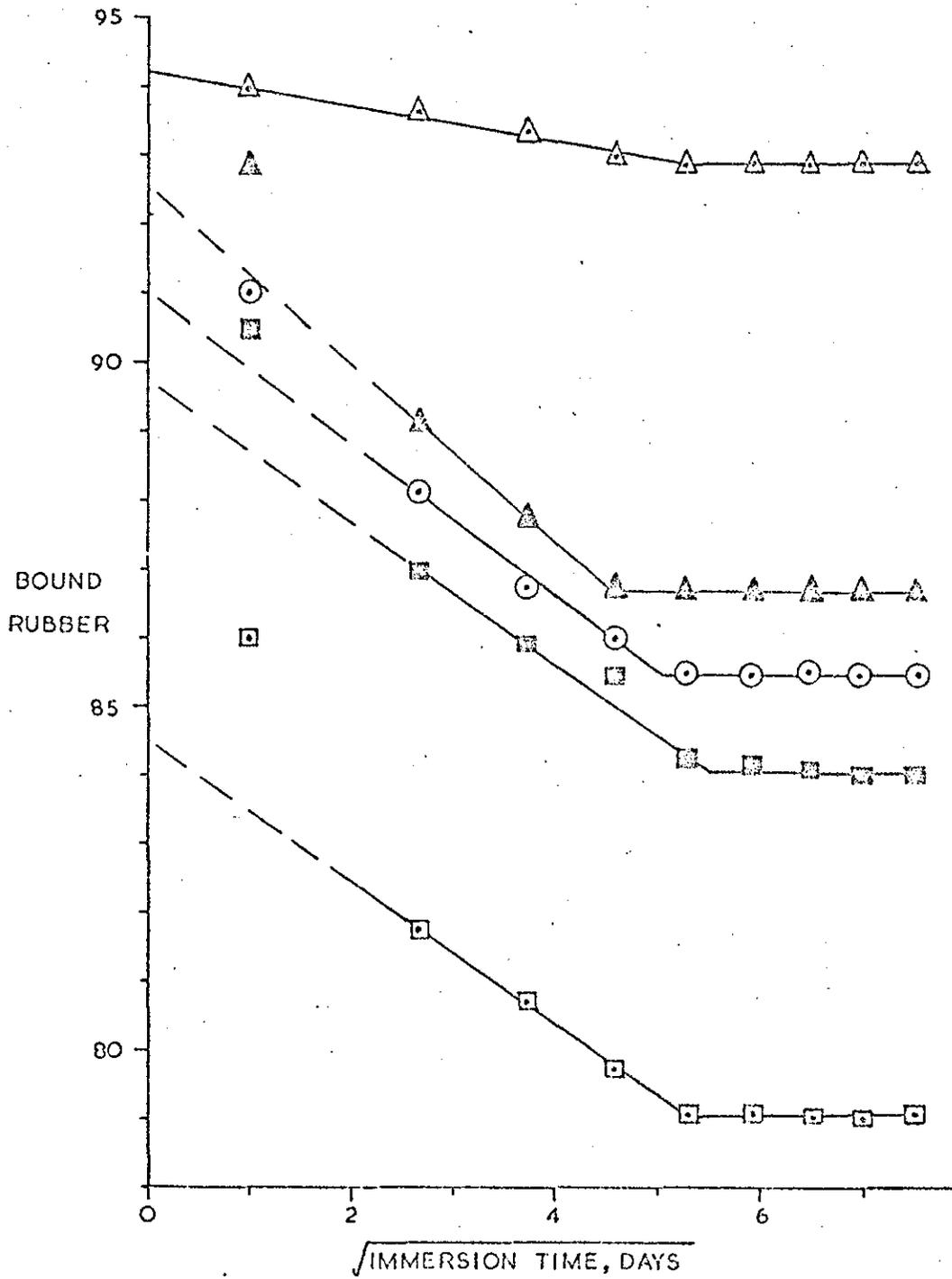


Figure 4.12 Dependence of bound rubber on the square root of immersion time for E303 containing 32 phr of Aerosil 300 in various liquids (Δ acetone ○ toluene □ hexane ▽ methyl isobutyl ketone ■ tetrahydrofuran)

Except in acetone duplicate values (Table 4.9) confirmed the effect of drying down as they were much lower following continuous immersion for 8 weeks (with several transfers to fresh liquid): no change occurred during subsequent cycles of immersion and drying down, consistent with equilibrium having been achieved within the 8 weeks.

### 4.3 SWELLING IN TOLUENE

#### 4.3.1 Effect of immersion time (unvulcanised mixes)

The swelling ( $S_B$ ) values in Table 4.10 confirmed the decrease with increase of filler concentration and bin-ageing time, and indicated lack of equilibrium within 14 days. Similar values obtained at the same time as the bound rubber of Figure 4.1 indicated lack of equilibrium within 100 days immersion.

Equilibrium values (Table 4.11) obtained at the same time as the bound rubber of Table 4.2 also confirmed the decrease with increase of filler concentration and on bin-ageing; the values also decreased on heating confirming the acceleration of bin-ageing effects. As before they increased with increase of immersion time but they were also increased by remilling.

As with bound rubber the weight of a test-piece immersed in toluene was found to continue to increase beyond apparent equilibrium when examination times were of sufficient duration: the weight was proportional to the square root of immersion time but with a change of rate of increase after approximately 1 year (Figure 4.13).

Table 4.9 Effect of liquid and extraction conditions on the bound rubber of E303 containing 32 phr of Aerosil 300

Liquid	Interrupted immersion (8 weeks)	Continuous immersion (8 weeks)	Subsequent interrupted immersion (6 weeks)
Acetone	93.0	93.4	93.5
	92.8	93.2	93.2
Methyl isobutyl ketone	86.3	74.9	74.9
	87.0	76.0	76.2
Toluene	85.0	67.1	67.1
	85.9	67.5	67.4
Tetrahydrofuran	83.0	74.2	74.2
	85.1	73.9	73.7
Hexane	80.1	65.2	65.2
	78.0	64.4	64.5

Table 4.10 Swelling ( $S_B$ ) of E302 containing various concentrations of Aerosil 300.

Filler concentration, phr		16	24	32	40	48
Bin-ageing time, days	Immersion time, days					
1	1	NP	NP	805	756	575
	2	NP	NP	1188	881	548
	7	NP	NP	1315	962	624
	14	NP	NP	1475	942	693
7	1	958	835	659	453	360
	2	1320	1248	875	556	424
	7	2139	1671	1091	622	459
	14	2435	2152	1426	703	526
14	1	795	710	650	438	352
	2	1290	1060	779	484	360
	7	1896	1572	1022	539	423
	14	2292	2110	1334	612	482
30	1	760	750	615	401	328
	2	1274	982	748	478	352
	7	1632	1209	907	520	422
	14	2210	1774	1313	586	450

Table 4.11 Effect of filler concentration in E302, bin-ageing time and mix treatment on Swelling ( $S_B$ )

Bin-ageing time, days	Mix treatment	Immersion conditions*	Filler concentration, phr						
			8	12	16	24	32	40	48
0	mixed only	1	NP	3156	3353	2366	1433	1022	841
		equilibrium	NP	NP	NP	NP	7740	NP	1148
	heated	1	917	689	597	424	280	265	294
		equilibrium	806	861	646	451	315	264	220
	remilled	1	NP	1278	1055	1178	819	675	659
		equilibrium	NP	NP	NP	NP	1464	939	1045
84	mixed only	1	806	741	623	406	299	246	215
		equilibrium	1456	985	834	519	392	294	283
	heated	1	850	631	516	434	248	231	195
		equilibrium	1030	783	635	428	410	233	400 (?)
	remilled	1	1233	821	680	525	365	315	229
		equilibrium	1948	1168	897	645	425	390	272

\* Immersion 1 day: single test-pieces  
 Conditions equilibrium: four test-pieces (median value quoted)

heat treatment: 4 hours at 250°C

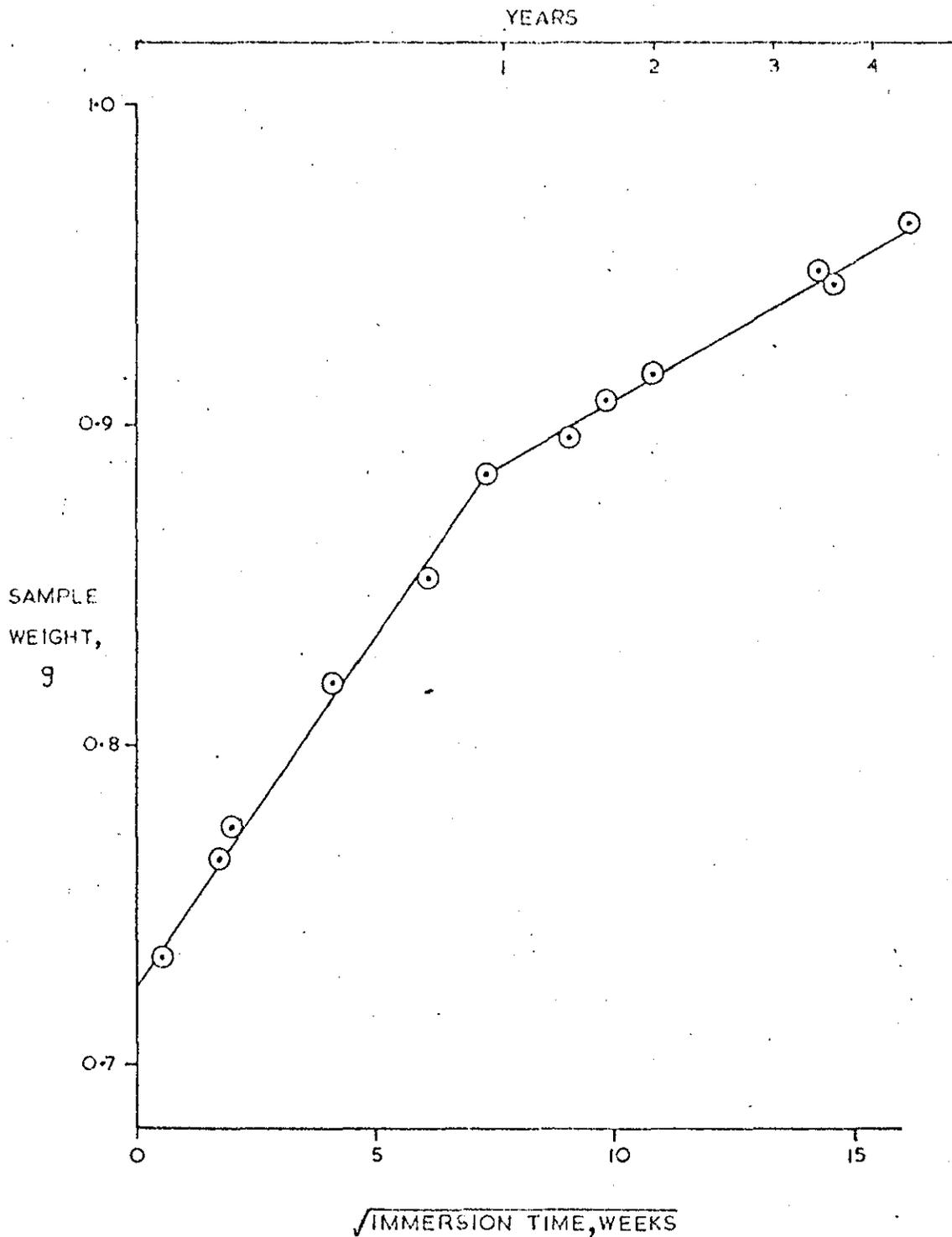


Figure 4.13 Dependence of the weight of E302 containing 26 phr of Aerosil 300 on the square root of immersion time

#### 4.3.2 Effect of immersion time (gum vulcanisate)

Although mean swelling ( $S_B$ ), of duplicate portions of an E303 vulcanisate (0.5 phr of peroxide) determined successively, exhibited considerable scatter when plotted against the square root of the immersion time, there was a very considerable increase within the first 1 day of immersion, followed by some further increase for 7 to 10 days (Figure 4.14).

#### 4.3.3 Effect of bin-ageing

There was a rapid decrease in swelling ( $S_B$  - 1 day immersion) of E303 containing 32 phr of Aerosil 300 within the first week of bin-ageing but the values lay on a curve when plotted against the square root of the post-reaction time as estimated in section 4.1.3 (Figure 4.15).

Morpholine accelerated the decrease in swelling ( $S_B$ ) of the mix with only 8 phr of Aerosil 300 (Table 4.12) and reduced the equilibrium value: the low concentration again probably accounted for the scatter of the values.

The E303 containing 32 phr of Aerosil 300 and 0.1 phr of morpholine, and found to be reprocessable after storage over morpholine was found to have a swelling ( $S_B$ ) of approximately 1500, compared with values in the absence of morpholine of approximately 1400 immediately after mixing reducing to approximately 300 on prolonged bin-ageing.

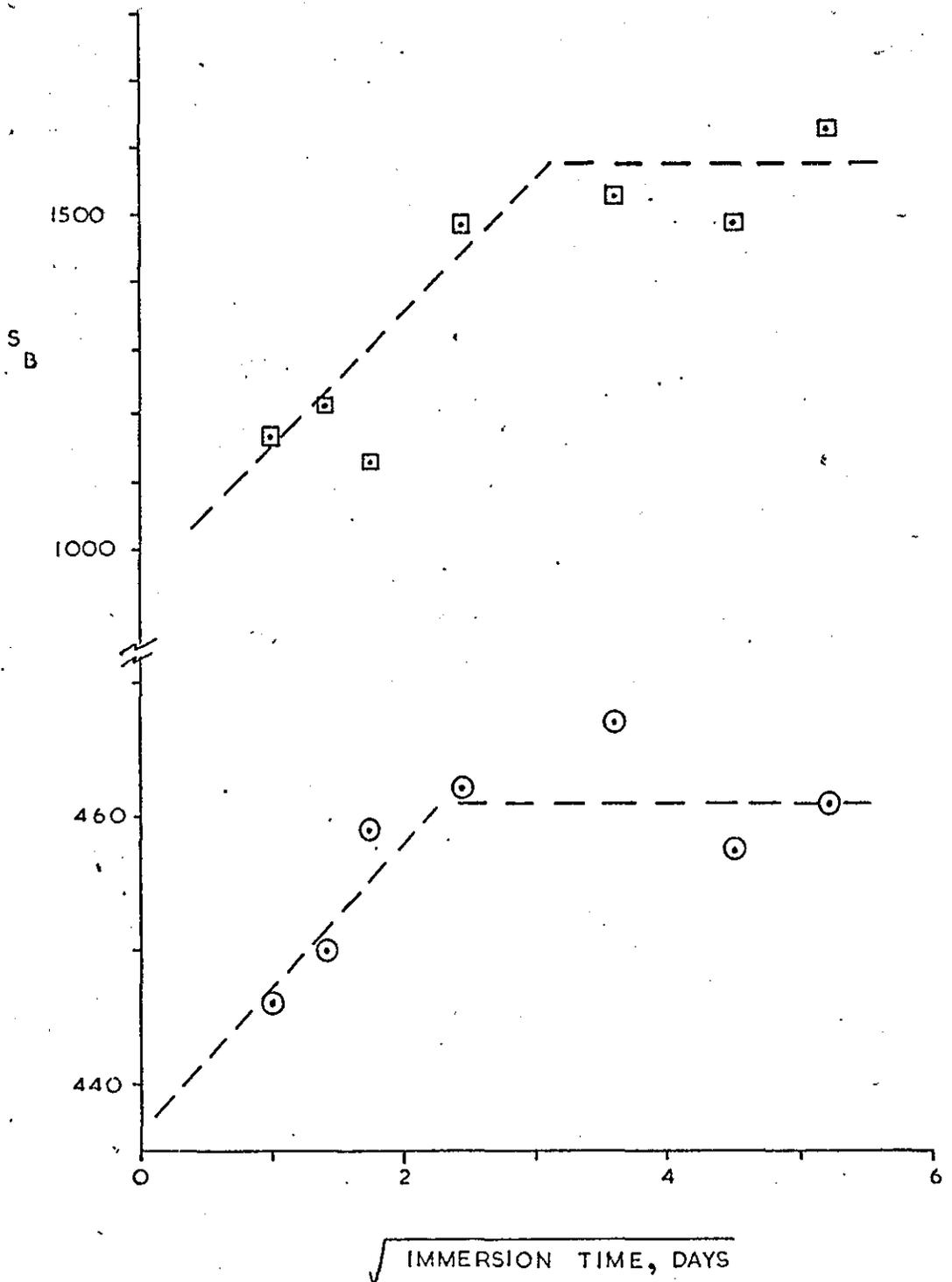


Figure 4.14 Dependence of swelling ( $S_B$ ) of "bound rubber" of E303 vulcanisates on the square root of immersion time (Peroxide concentration ○ 0.5 phr □ 0.2 phr)

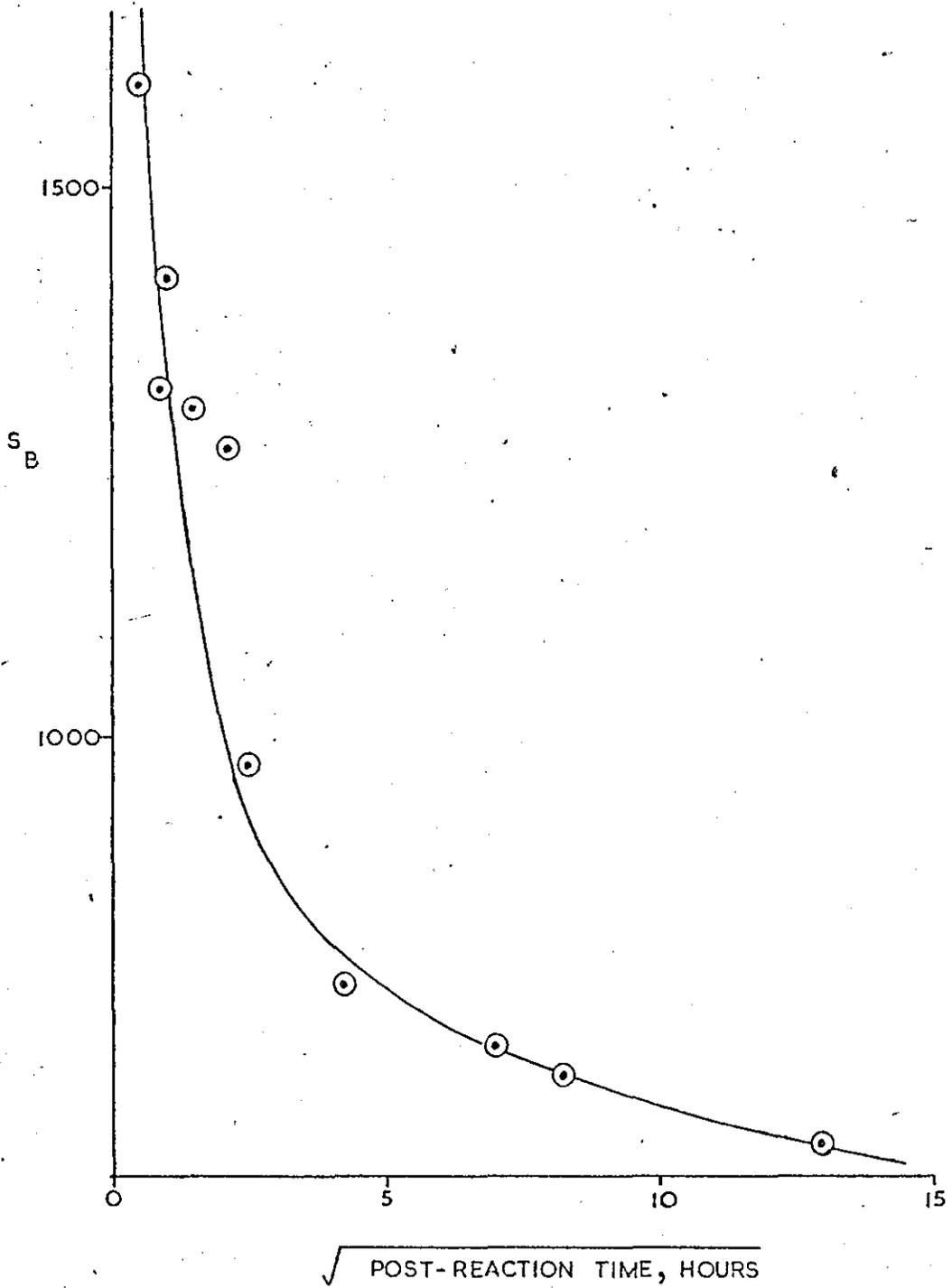


Figure 4.15 Dependence of swelling ( $S_B$ ) on the square root of bin-ageing time, of E303 containing 32 phr of Aerosil 300, after allowance for interaction occurring during mixing

Table 4.12 Effect of morpholine on the swelling ( $S_B$ ) of E303 containing 8 phr of Aerosil 300

Morpholine concentration, phr	Nil	0.1
Bin-ageing time, days		
0	2022	1280
1	1223	1012
2	1151	974
3	1110	870
7	1182	862
10	1030	984
14	1006	917
28	1031	852
36	1000	899
49	1020	870

#### 4.3.4 Effect of filler type and concentration

The values in Tables 4.10 and 4.11 confirmed the decrease in swelling ( $S_B$ ) with increase in concentration of Aerosil 300.

Typical values illustrative of the decrease in swelling ( $S_B$  - 1 day immersion) with increase in specific surface area of untreated silica, and the higher swelling of a treated silica mix are given in Table 4.13.

#### 4.3.5 Osmotic pressure effect

The swelling values ( $S_B$ ) of the E303 vulcanisate (0.5 phr of peroxide) were linearly related to the final solution concentration after immersion for 2 days (Figure 4.16). Although the swelling values ( $S_B$  - 1 day immersion) of E303 freshly mixed with 32 phr of Aerosil 300 also decreased with increase of final solution concentration, there was no direct proportionality (Figure 4.16).

### 4.4 SWELLING IN OTHER LIQUIDS

#### 4.4.1 Gum vulcanisate

Successive swelling values ( $S_B$ ) were obtained on immersion of the E303 vulcanisate (0.5 phr of peroxide) but these were converted to volume values ( $V_B$ ) to show more distinctly the differences between liquids when plotted against the square root of immersion time (Figure 4.17): the values decreased as the solubility parameter of the liquids increased from the similar values of hexane and silicone rubber.

Table 4.13 Effect of fillers (32 phr) and bin-ageing on the swelling ( $S_B$  - 1 day immersion) of E303

Filler	Bin-ageing time, days		
	0	2	7
EP 154	NP	1375	1301
Aerosil 300	1056	632	446
Aerosil 200	1405	713	503
Celite Superfloss	NP	NP	NP

NP test-pieces disintegrated

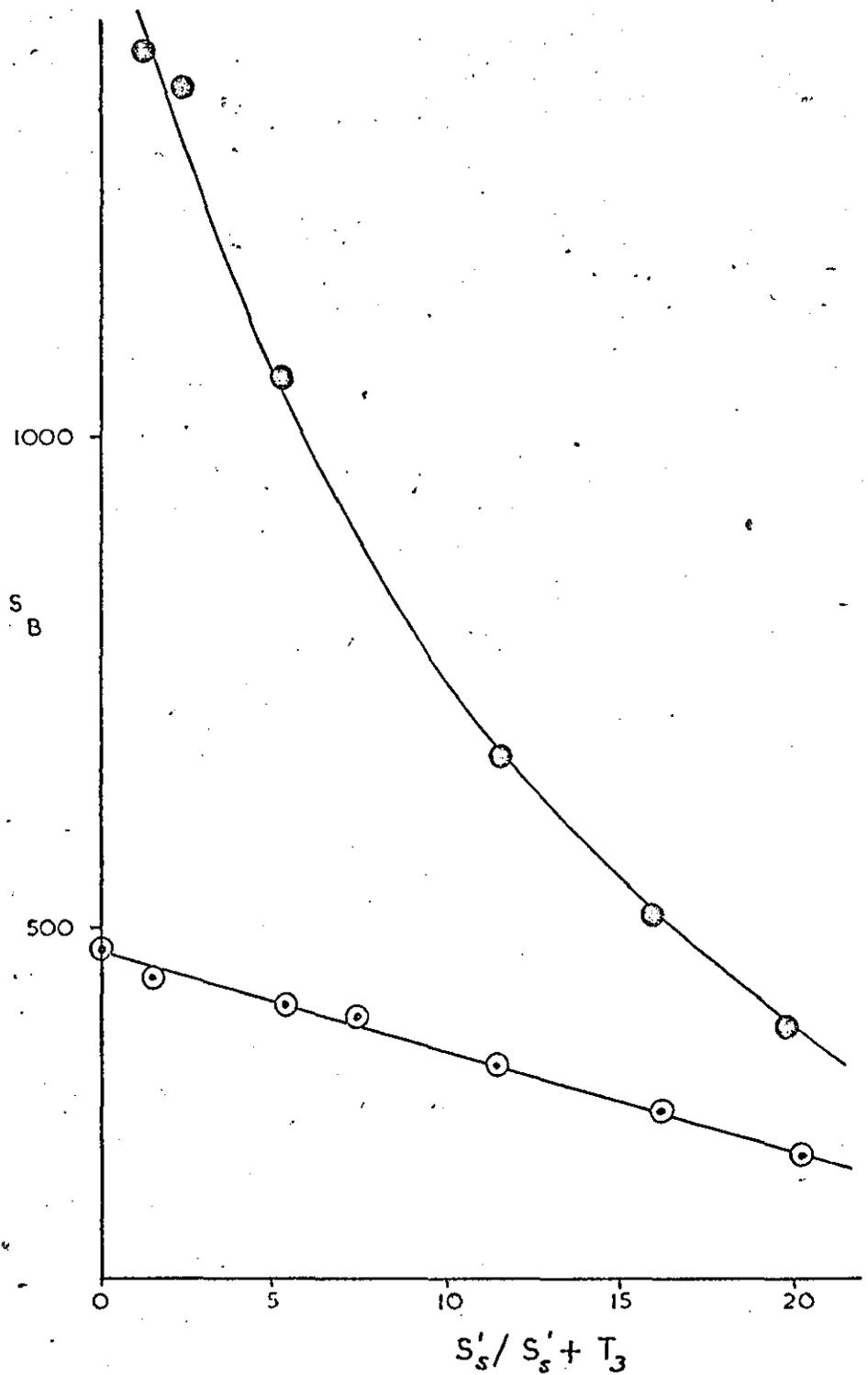


Figure 4.16 Dependence of swelling ( $S_B$ ) on the final concentration of E303 in toluene

⊙ E303 vulcanisate (0.5 phr of peroxide): immersed for 2 days

⊗ E303 containing 32 phr of Aerosil 300 (BAT=0): immersed for 1 day

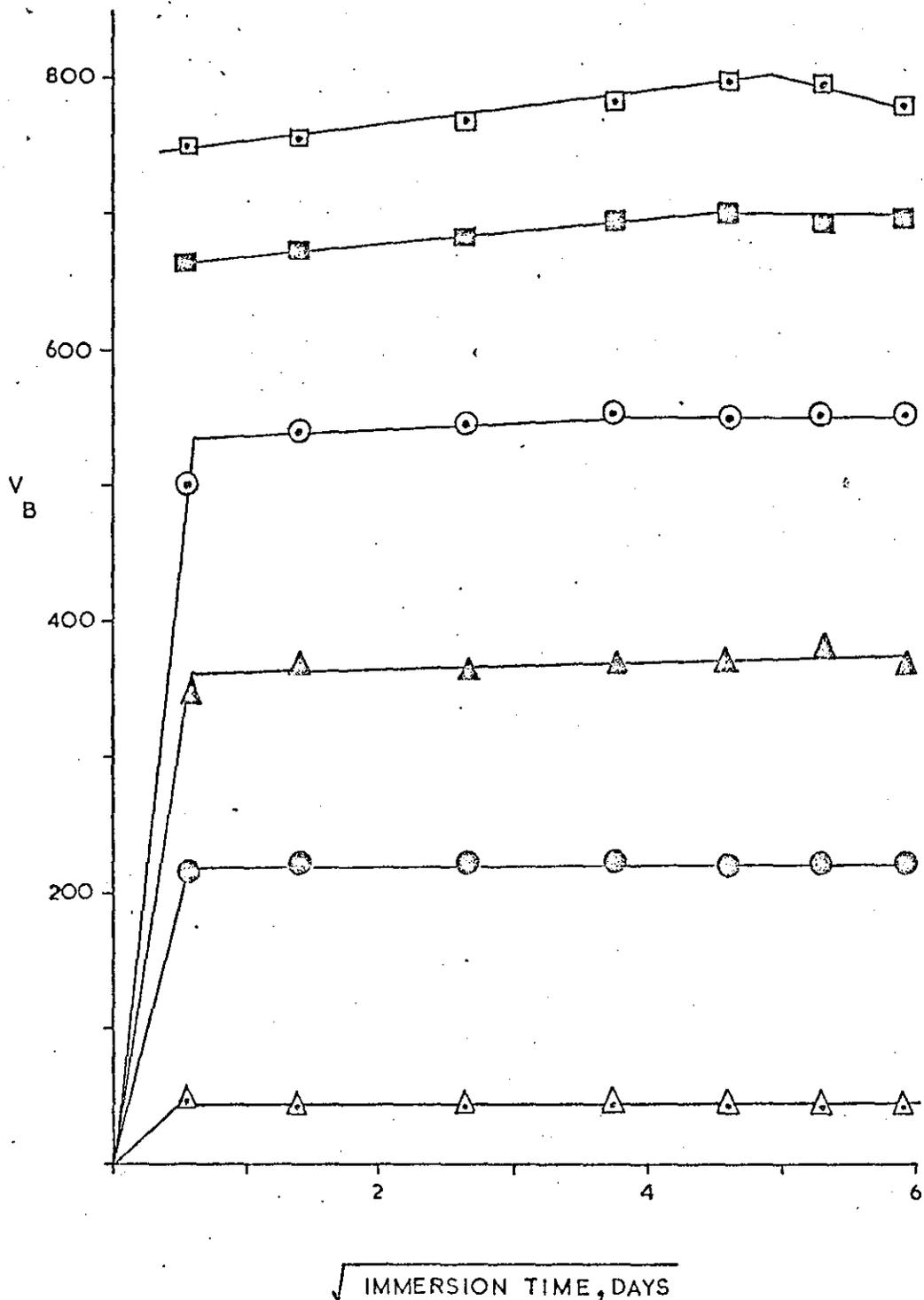


Figure 4.17 Dependence of swelling ( $V_B$ ) of an E303 vulcanisate (0.5 phr of peroxide) on the square root of immersion time and liquid ( $\Delta$  acetone  $\circ$  toluene  $\square$  hexane  $\Delta$  methyl isobutyl ketone  $\circ$  methyl ethyl ketone  $\square$  tetrahydrofuran)

Because test-pieces had the liquid removed between determinations, swelling might easily have been dependent on the time between the determinations rather than on the total immersion time, yet the values in hexane still appeared to be related to the latter rather than to the former. Irrespective of this factor, swelling was dependent on the liquid but on transfer to hexane all test-pieces attained the same equilibrium value of  $799 \pm 10$ : this established that there was no basic change on removal of the liquid; similarly, values obtained after continuous immersion for 7 weeks (with several transfers to fresh liquid) were within 10 of the maximum values in Figure 4.17.

#### 4.4.2 Filled mix

Swelling values ( $V_B$ ) of E303 containing 32 phr of Aerosil 300 (bin-aged for 3 weeks at  $8^\circ\text{C}$ ) were obtained successively and the final values (8 weeks) were compared with values after transfer to hexane for 4 weeks: they were further compared with values obtained after uninterrupted immersion for 8 weeks (with several transfers to fresh liquid), after a further 6 weeks (interrupted) immersion and after 4 weeks immersion in hexane (Table 4.14).

As with bound rubber, swelling revealed that the removal of liquid led to further interaction between rubber and filler but the difference between the final two sets of results in hexane indicated that the effect of drying down was itself dependent on immersion history. Apparently the changes occurring during continuous immersion in liquid

Table 4.14 Effect of liquid and immersion conditions on the swelling ( $V_B$ ) of E303 containing 32 phr of Aerosil 300

Liquid	Toluene	MIBK	THF	Hexane	Acetone
	Immersion conditions				
8 weeks* interrupted immersion	503	390	657	666	52
4 weeks after transfer to hexane	578	550	564	-	505
8 weeks uninterrupted immersion	828	494	823	1099	54
6 weeks interrupted immersion after last line	549	380	590	703	49
4 weeks after transfer to hexane	732	750	617	679	684

\* no change between 6 and 8 weeks

partially protected the system from the changes on subsequent drying down: these differences could not be attributed to the differences in periods of interrupted immersion as there was no significant change between 6 and 8 weeks.

#### 4.5 MOLECULAR WEIGHT OF SOL RUBBER

Molecular weight, determined on the solution after 2 day immersion of E303 containing 8 phr of Aerosil 300, showed an increase on bin-ageing, both in the absence and presence of morpholine (Table 4.15). The initial extract in the absence of morpholine, amounting to 84% of the polymer (Section 4.1.3), was apparently unchanged E303; as the amount of sol decreased the increase in molecular weight indicated selective adsorption of low molecular weight components from a polymer with wide molecular weight distribution.

Similarly, the molecular weight of the sol rubber extracted from the mix containing morpholine increased on bin-ageing: however, the bound rubber was independent of bin-ageing time and exceeded the highest value in the absence of morpholine (Section 4.1.3). The change in the molecular weight was, therefore, more significant and implied displacement of high molecular weight polymer by lower molecular weight polymer, on the filler surface, contrary to the normal stability of the former (Duke, Taft and Kolthoff 1951). In the case of silicone rubber, however, there is the possibility of siloxane bond

Table 4.15 Effect of morpholine on the molecular weight  $\times 10^{-6}$  of sol rubber extracted from E303 containing 8 phr of Aerosil 300

Bin-ageing time, days	Morpholine concentration, phr	
	Nil	0.1
0	0.64	0.48
3	0.71	0.56
8	0.77	0.64
16	0.85	0.74
28	0.86	0.75

E303 0.64

rearrangement etc upsetting normal adsorption phenomena, especially in the presence of morpholine, to favour the adsorption of lower molecular weight polymer.

Final remilling of E303 containing 32 phr of Aerosil 300, successively bin-aged and remilled to low viscosity, only changed the sol rubber from 4% with a molecular weight of  $0.75 \times 10^6$  to 6% with a molecular weight of  $0.73 \times 10^6$ : thus the small quantity of polymer remaining unadsorbed was not low molecular weight material where many adsorption sites would be required to bind it.

Sol rubber obtained from immersion of an E303 vulcanisate (0.2 phr of peroxide) in acetone for 4 days, and then for a further 8 days, had a constant molecular weight of  $0.35 \times 10^6$ : further sol rubber, extracted by immersion for 1 day in hexane, had a molecular weight of  $0.48 \times 10^6$ , compared with  $0.64 \times 10^6$  for the original polymer. As it had already been established that hexane extracted more rubber than did acetone (Section 4.2.1), and gave higher swelling (Section 4.4.1), it appeared possible that the two effects were related: perhaps the polymer-polymer, or polymer-filler, networks were having a molecular sieve type effect on the matrix rubber molecules. Earlier evidence of a linear relationship between bound rubber and swelling was mentioned in Section 1.3.

#### 4.6 BOUND RUBBER-SWELLING CORRELATION

The linear relationship between bound rubber (Table 4.1) and swelling (Table 4.10) was confirmed for E302 containing high concentrations of Aerosil 300 (Figure 4.18), with variation in both bin-ageing time and immersion time; this is shown more clearly in Figure 4.19. Similar linearity was obtained between bound rubber (Table 4.4) and swelling (Figure 4.15) after only limited bin-ageing (Figure 4.20).

Similar lines were obtained for remilled mixes on varying the immersion time (Figure 4.21) but they were displaced in the direction of lower swelling for given bound rubber. Similar displacement was observed when a mix was subjected to more severe milling at the mixing stage (Figure 4.22).

Although these results confirmed the earlier correlation between bound rubber and swelling ( $S_B$ ), the slope and position of the lines, and the effect of remilling, were somewhat different. This is attributed to a change in the rate of formation and alteration of network structure: such a change could also account for small differences in various effects, such as a reduced tendency for mixes to crepe-harden.

However, it was observed that, in some determinations, the amount of liquid absorbed was nearly independent of immersion time: this could be the source of a correlation between swelling ( $S_B$ ) and bound rubber although the

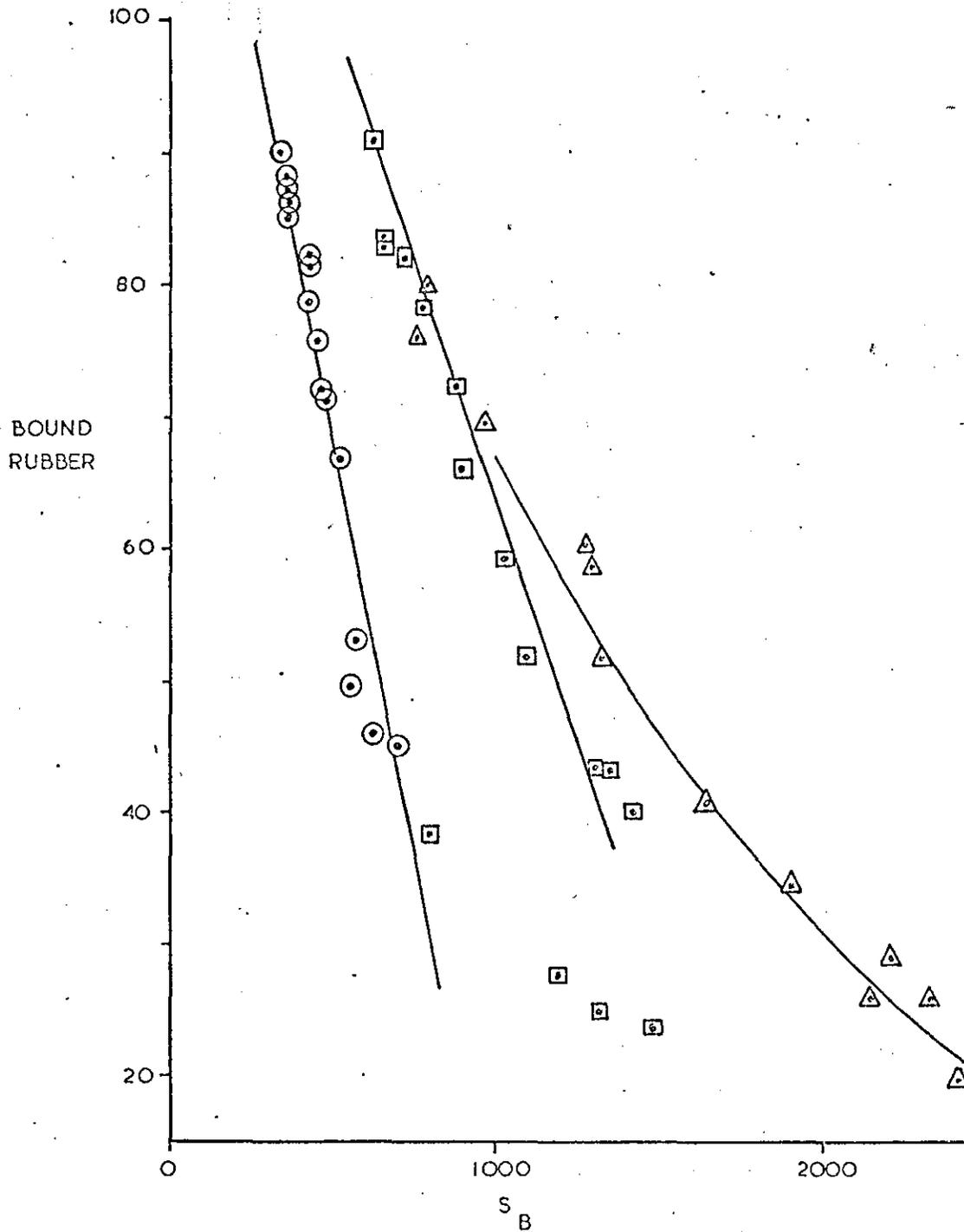


Figure 4.18 Relationship between bound rubber and swelling ( $S_B$ ), with variation of bin-agein time and immersion time, of E302 containing Aerosil 300  
 (⊙ 48 phr   ⊠ 32 phr   Δ 16 phr)

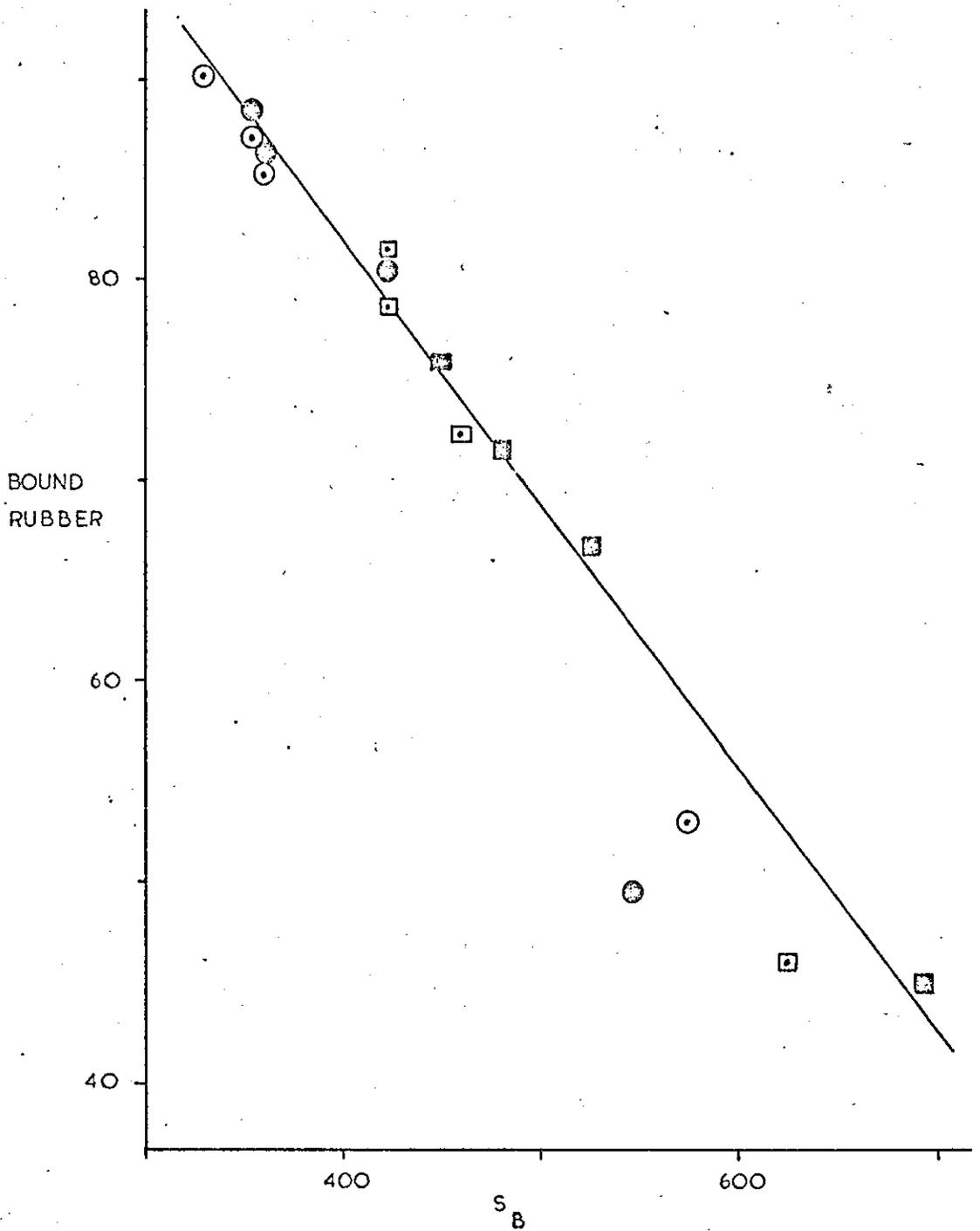


Figure 4.19 Data from Figure 4.18, for E302 containing 48 phr of Aerosil 300, to illustrate the effect of immersion time, days  
 (○ 1 ● 2 □ 7 ■ 14)  
 and bin-ageing time (1 to 30 days)

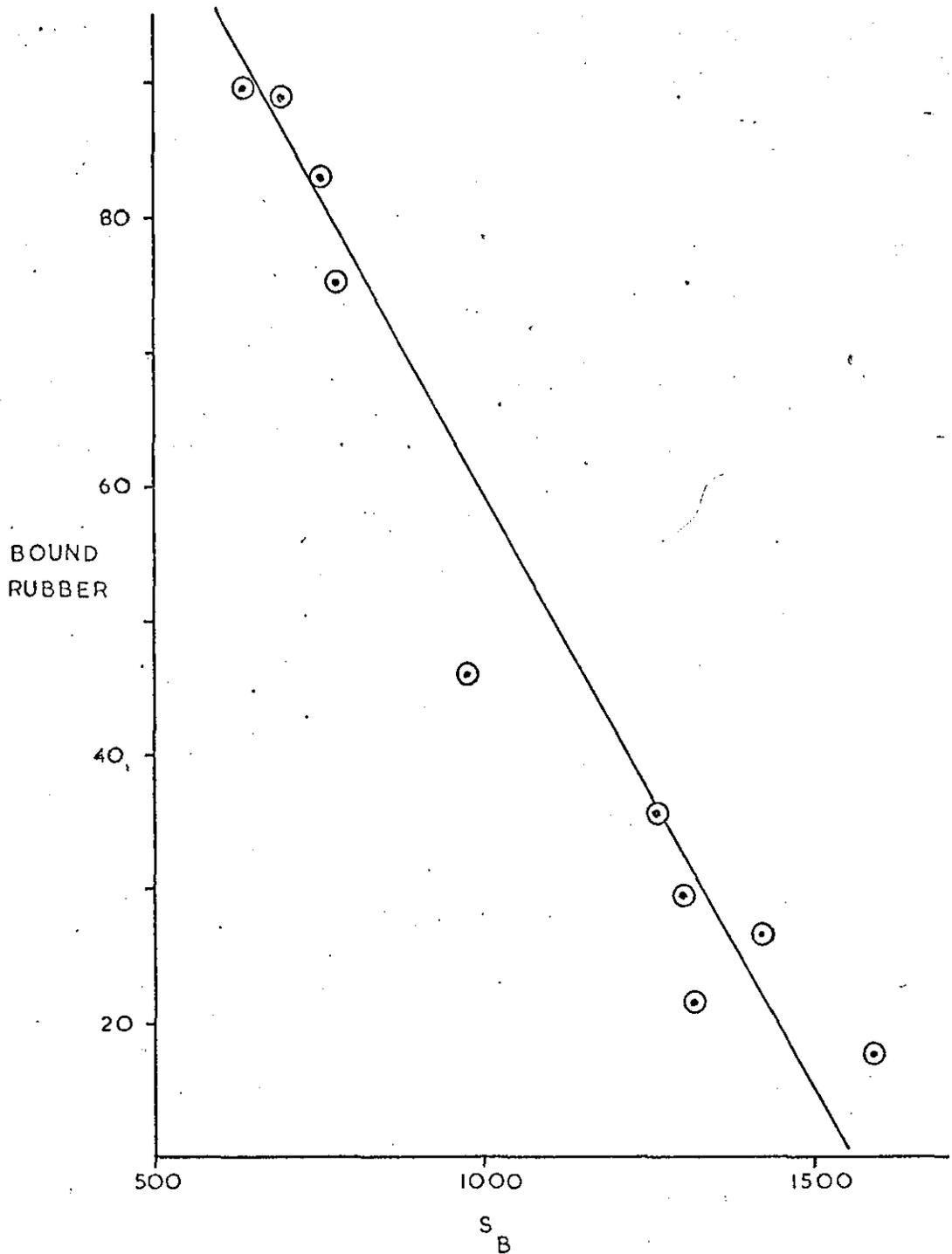


Figure 4.20 Relationship between bound rubber and swelling ( $S_B$ ) for freshly mixed E303 containing 32 phr of Aerosil 300 (Data from Table 4.4 and Figure 4.15)

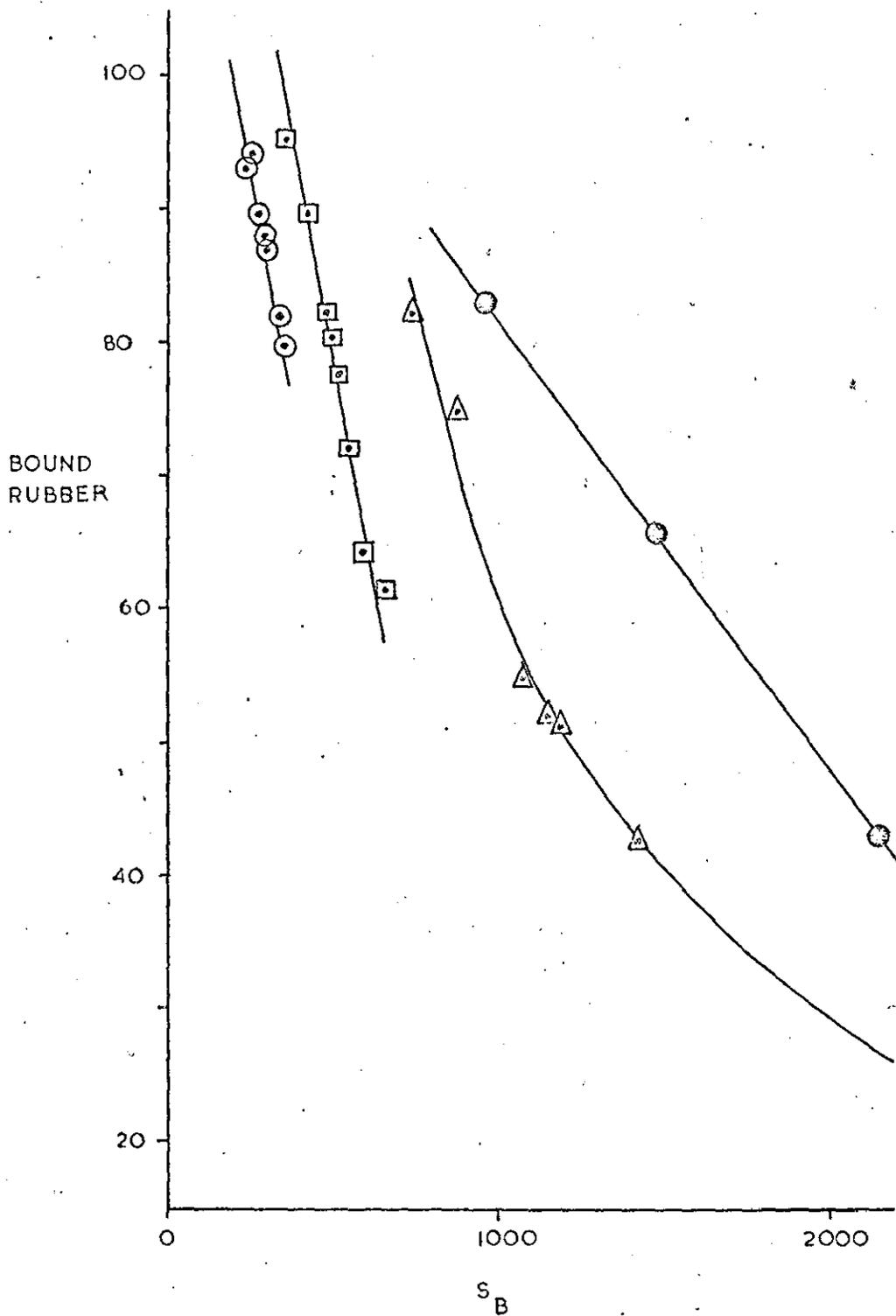


Figure 4.21 Relationship between bound rubber and swelling ( $S_B$ ), with variation of immersion time, of (remilled) E302 containing Aerosil 300  
 (○ 48 phr □ 32 phr △ 16 phr ● 8 phr)

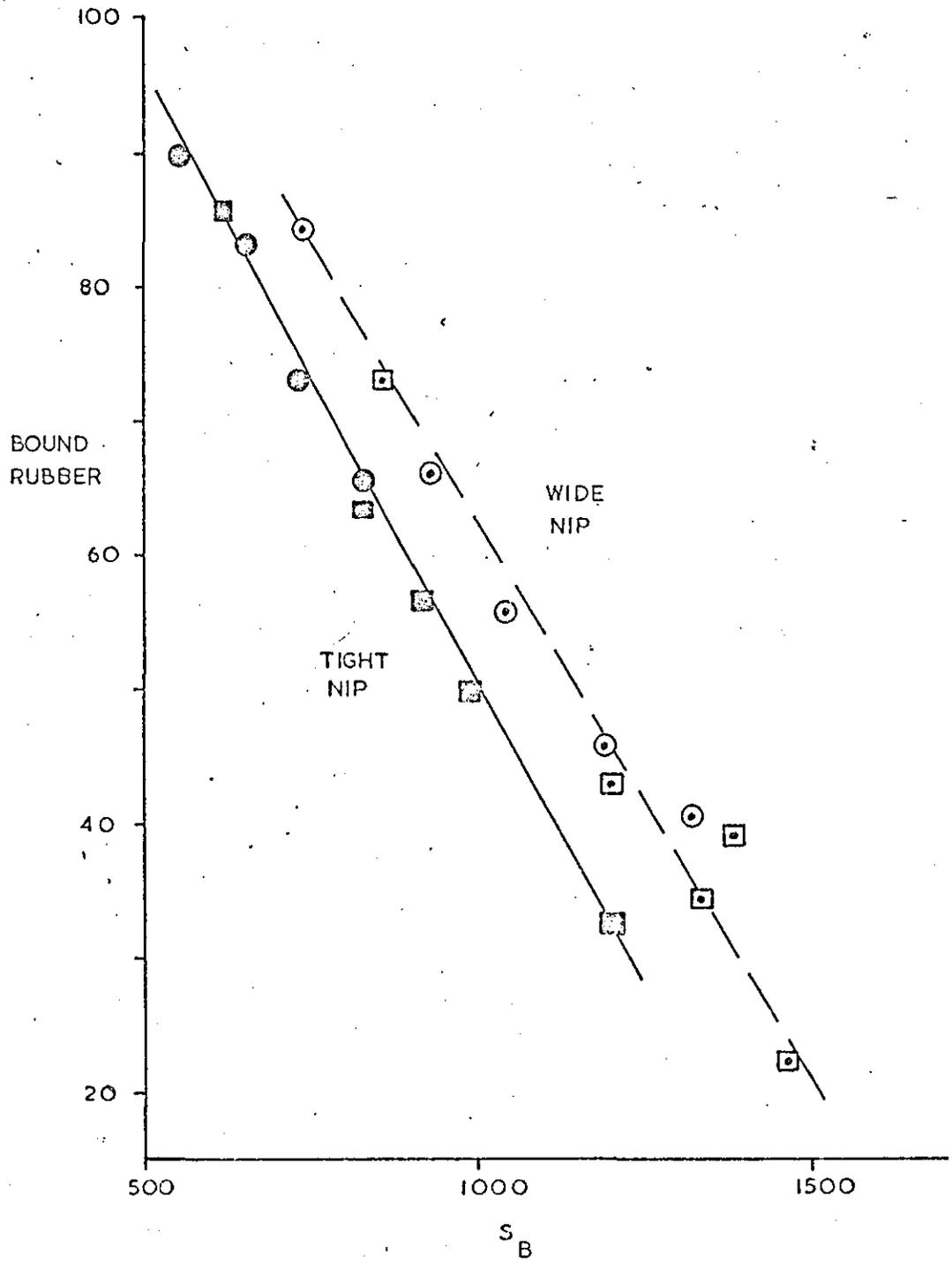


Figure 4.22 Effect of mill nip on the relationship between bound rubber and swelling ( $S_B$ ) (Bin-ageing time  $\square$   $\blacksquare$  1 week  $\circ$   $\odot$  2 weeks)

relationship should be one of reciprocity and not of direct proportionality.

#### 4.7 LIQUID ABSORPTION

The bound rubber of Figure 4.1 was replotted (Figure 4.23) with the liquid absorbed related to the original mix weight (i.e.  $S_M$ ) instead of to the unextracted polymer weight (i.e.  $S_B$ ). There was a clear tendency for the relationship to be dependent on filler concentration, ranging from a typical swelling increment at high concentration to the opposite at low filler concentration: the "abnormal" values at the shortest immersion time were presumably due to non-attainment of "equilibrium".

The bound rubber of Table 4.1 was similarly replotted but with variation of both bin-ageing time and immersion time the picture was more complicated: nevertheless it was similar to the previous one particularly when the values after only 1 day bin-ageing were excluded: these had low values of both bound rubber and liquid absorption. The tendency for values at low bin-ageing time to be different was better shown (Figure 4.24) when the values from Figure 4.20 were replotted in the same way.

The correlation between bound rubber and swelling in Section 4.6 could not therefore be attributed solely to a constancy of liquid absorption: on the other hand, any non-equilibrium values of bound rubber must be treated with caution. Using the only set of equilibrium

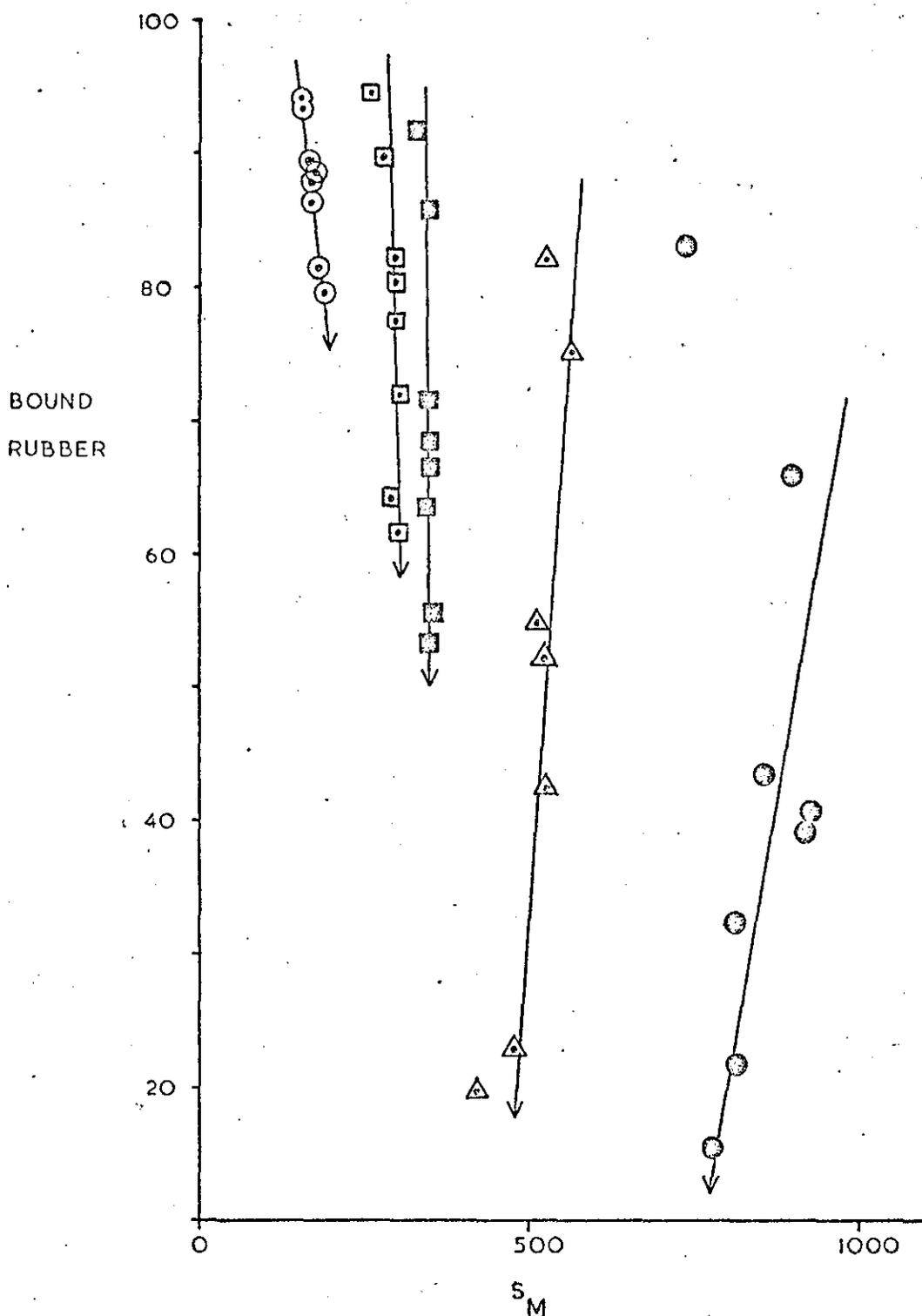


Figure 4.23 Relationship between bound rubber and liquid absorption ( $S_M$ ), with immersion time increasing in the direction arrowed, for E302 containing Aerosil 30 (● 48 phr □ 32 phr ▣ 24 phr △ 16 phr ○ 8 phr)

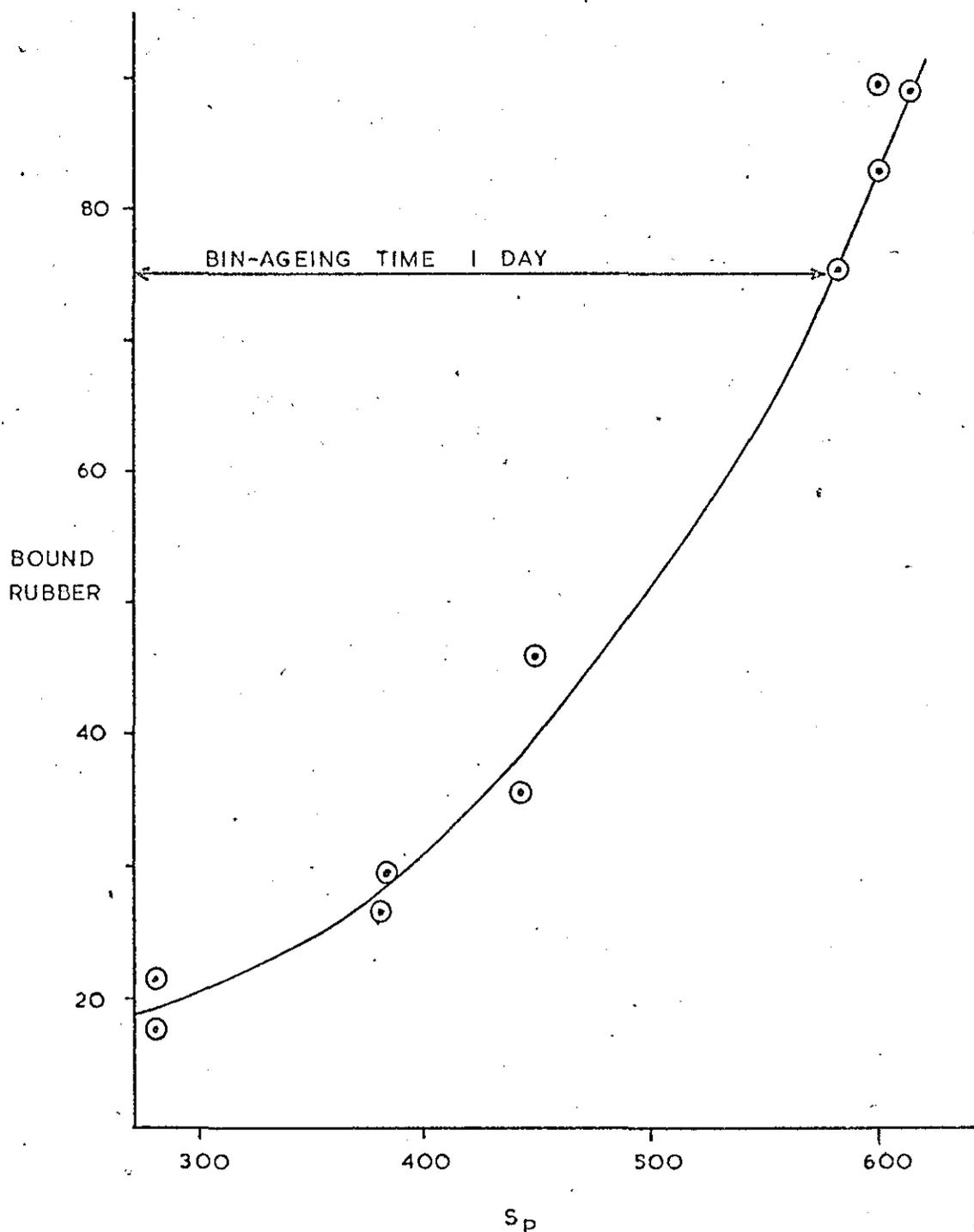


Figure 4.24 Relationship between bound rubber and liquid absorption ( $S_p$ ) for freshly mixed E303 containing 32 phr of Aerosil 300 (compare Figure 4.20)

values for unvulcanised mixes (Tables 4.2 and 4.11) the plot of bound rubber against liquid absorption per unit weight of initial rubber ( $S_p$ ) gave a fair approximation to a straight line (Figure 4.25) establishing some correlation between liquid absorption and bound rubber, at least for the filler concentration range of 12 phr to 48 phr.

Strictly even these values were not equilibrium ones as the swelling increased for a very long time (Figure 4.23). Extrapolation of the lines of Figure 4.23 to much longer immersion times suggested eventual convergence on a value of approximately 20% bound rubber, with an  $S_M$  value of approximately 350, and thus of the same order as for a freshly prepared mix (Figure 4.24). In the other direction extrapolation to 100% bound rubber gave values of swelling ( $S_M$ ) which when converted to relate to polymer content ( $S_p$ ) were almost directly proportional to the logarithm of the filler concentration (Figure 4.26).

With the gum vulcanisate (0.5 phr of peroxide) bound rubber decreased on immersion to an equilibrium value but the volume of liquid absorbed was nearly constant after 7 hours immersion. The bound rubber was not directly related to the volume of liquid absorbed but there was a tendency for the former to decrease as the latter increased.

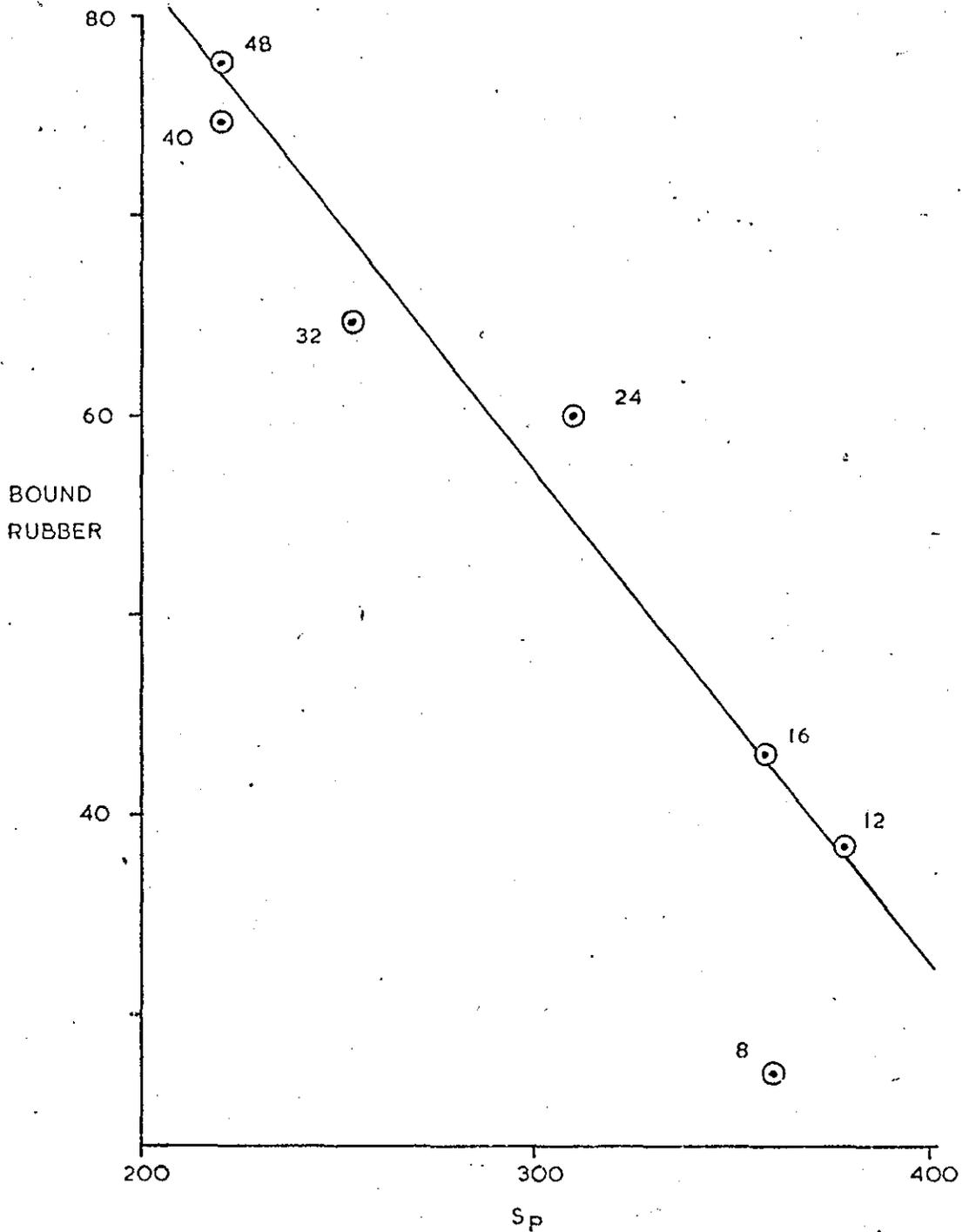


Figure 4.25 Relationship between equilibrium bound rubber and liquid absorption ( $S_p$ ) for E302 containing the quoted concentrations of Aerosil 300, phr

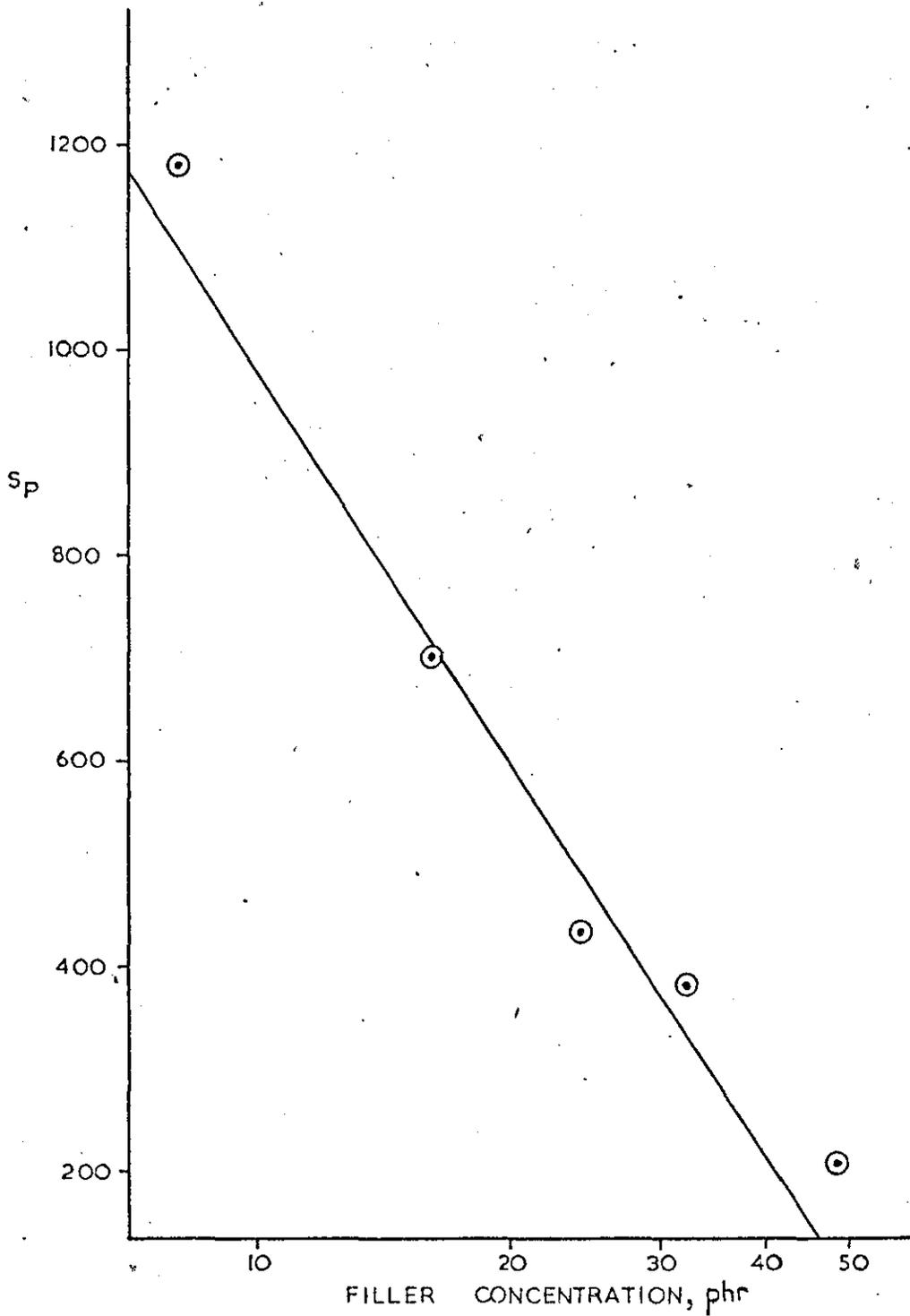


Figure 4.26 Relationship between liquid absorption ( $S_p$ ), calculated from the lines in Figure 4.23 extrapolated to bound rubber = 100, and concentration of Aerosil 300 in E302

#### 4.8 CONCLUSIONS

The ability of a piece of an unvulcanised silicone rubber-silica mix to maintain its shape when immersed in a powerful solvent for the rubber is indication of considerable interaction. The insolubility of some of that rubber, sometimes a large amount of that rubber, is further evidence of such interaction. Short of all the rubber being extracted, and extrapolation of the line in Figure 4.3 implies that it would take approximately 20 years, there must still be some network structure and, again, this seems unlikely to be solely filler-filler structure.

The activation energy of bound rubber formation immediately after mixing provides further evidence of a chemical reaction between silicone rubber and Aerosil 300. The proportionality to the square root of time, often observed in the changes during bin-ageing and during immersion in liquid, indicates a dependence on diffusion rates. Taken together these provide support for the suggestion in Section 3.7 that the interaction is chemical in nature but often controlled by the rate of diffusion of the polymer to the filler.

The increase in bound rubber with increase of filler reactivity, filler concentration and bin-ageing time is consistent with the fairly widely held view that bound rubber is a useful indicator of reinforcement: indeed, bound rubber appears to be exponentially dependent on filler concentration (Figure 4.2). Nevertheless it is now proposed that bound rubber is only a secondary indicator.

The primary factor is now seen to be that which controls the expansion of the network in the presence of a liquid. It can also produce a constancy of liquid absorption, exponentially related to the filler concentration (Figure 4.26) but proportional to equilibrium bound rubber (Figure 4.25). Even in a gum vulcanisate the amount of soluble rubber extracted is dependent on the solubility parameter of the liquid and thus on the expansion of the network by the absorbed liquid (Figure 4.27).

These conclusions are not in conflict with those of Gessler (1969) who claimed that the bound rubber of butyl rubber-carbon black mixes was virtually independent of solvent type: there was a slight decrease in bound rubber as swelling increased but the main difference was that swelling was much higher than in the present work, ranging from 2,000 - 12,000 (%).

It is now proposed that the primary factor is the three-dimensional structure comprising filler particles and interparticular rubber; this can be likened to the three-dimensional structure of polymer chains and crosslinks in a vulcanisate for which liquid absorption is often used to determine crosslink density.

The amount of liquid absorbed by the filler-interparticular rubber network will depend on the average length of interparticular rubber between filler particles and

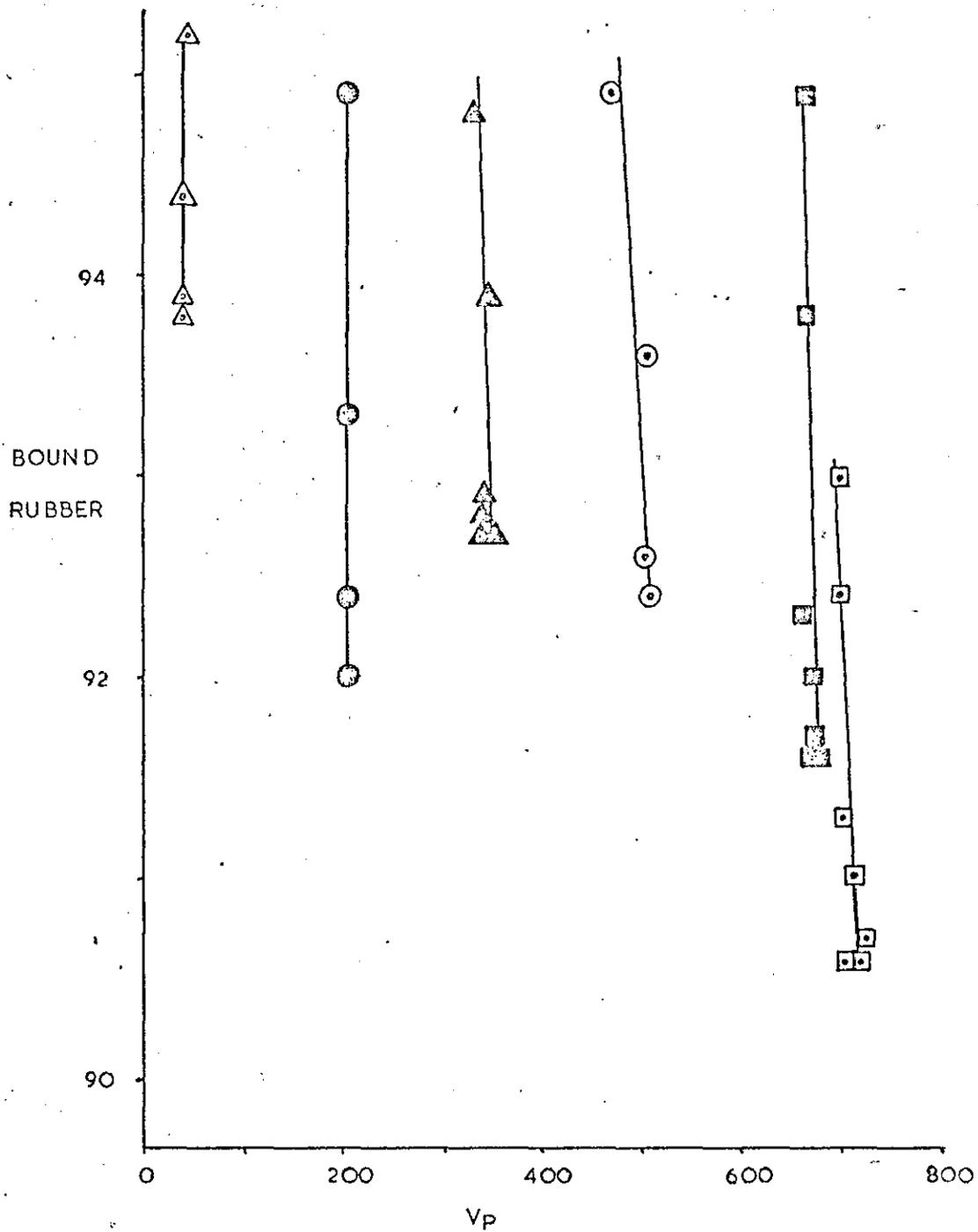


Figure 4.27 Relationship between "bound rubber" and the volume of liquid absorbed per 100 volumes of initial polymer ( $V_p$ ) ( $\Delta$  acetone  $\odot$  toluene  $\square$  hexane  $\blacktriangle$  methyl isobutyl ketone  $\odot$  methyl ethyl ketone  $\blacksquare$  tetrahydrofuran)

thus, to a large extent, on the distance between filler particles: it will not be affected by the amount of interparticular rubber once the network is firmly established. At low bin-ageing times it may be affected by the absorption behaviour of a high concentration of matrix rubber while, at high bin-ageing times, it may be affected by changes in the interparticular rubber due to hydrolysis etc.

The bound rubber, as determined, will be the sum of the adsorbed rubber, interparticular rubber and residual matrix rubber: even the equilibrium bound rubber may contain residual matrix rubber if it cannot diffuse through the network "windows". The adsorbed rubber will not have much effect apart from reducing the amount of soluble rubber, particularly if it is closely associated with the filler surface; if it only has one adsorption site per molecule it will have a slight effect on the activity of the liquid within the gel.

## CHAPTER 5 STRESS-STRAIN PROPERTIES

### 5.1 YOUNG'S MODULUS AND HARDNESS

#### 5.1.1 Silicone rubbers

E302 containing 16 or more phr of Aerosil 300 exhibited elasticity when tested immediately after mixing; similar elasticity was exhibited by E302 containing only 8 phr of Aerosil 300 after bin-ageing for 105 days: elasticity was only exhibited over a limited strain range up to approximately 0.09 with 8 phr of Aerosil 200 and to 0.02 with 40 phr of Aerosil 300. Young's modulus increased on bin-ageing to a maximum value: this, like the value immediately after mixing, increased monotonically with increase of filler concentration (Figure 5.1). The time to the maximum was itself dependent on filler concentration, ranging from about 9 days with 40 phr of filler to more than 100 days with 8 phr of filler.

Young's modulus and apparent hardness of E302 containing 30 phr of Santocel FRC increased on bin-ageing (Table 5.1); apparent hardness showed the lesser scatter of values. Both properties appeared to be directly related to the logarithm of bin-ageing time and this is illustrated for apparent hardness (Figure 5.2).

The elasticity was attributed to interparticular rubber which, with the filler, gave a three-dimensional structure. The increase in Young's modulus and apparent hardness on bin-ageing was believed to be due to an increase in interparticular rubber and/or adsorbed rubber.

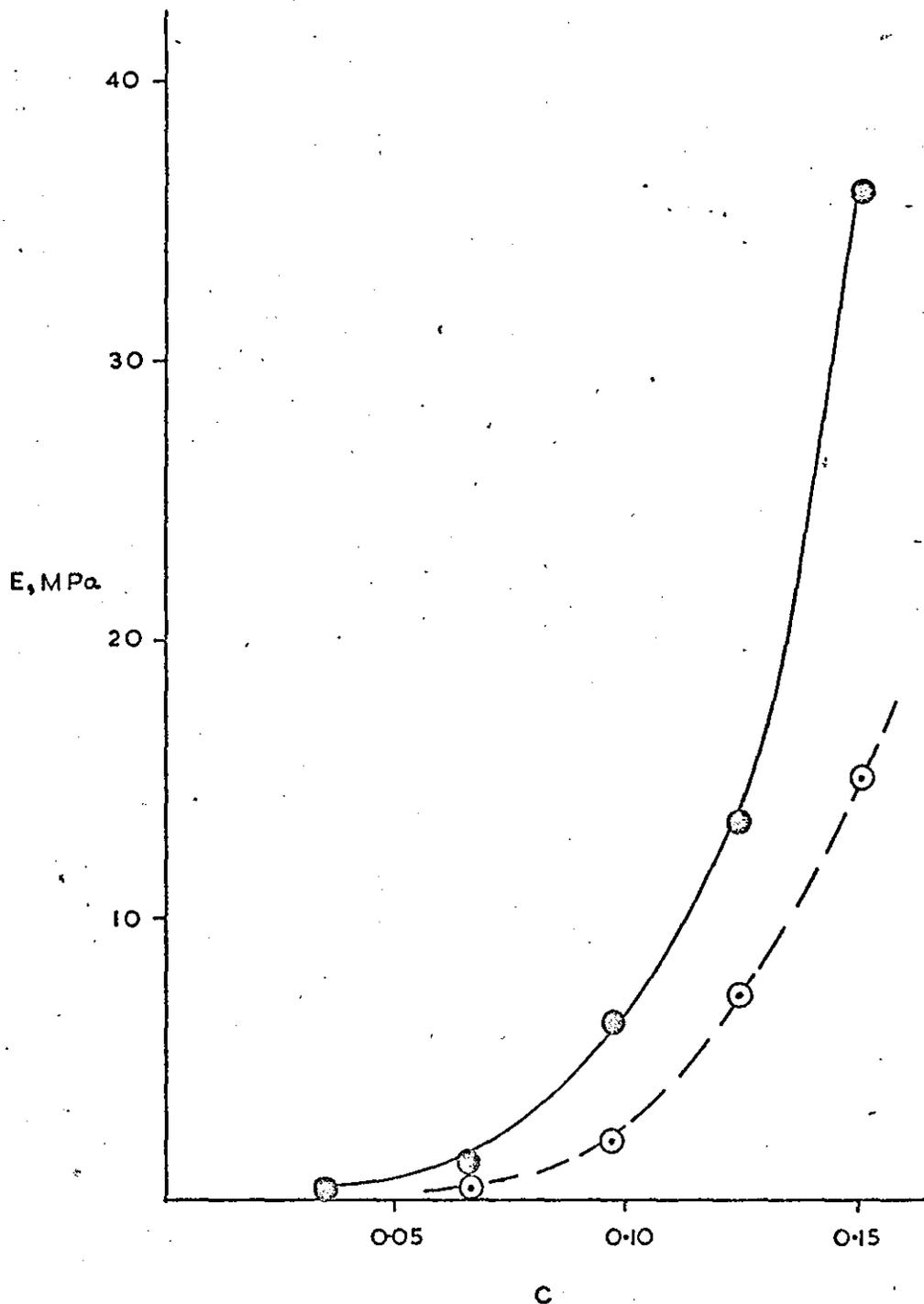


Figure 5.1 Dependence of Young's modulus ( $E$ ) of unvulcanised E302 on the volume concentration ( $c$ ) of Aerosil 300, immediately after mixing  $\odot$  and after bin-ageing to equilibrium  $\bullet$

Table 5.1 Effect of bin-ageing on the Young's modulus and apparent hardness of E302 containing 30 phr of Santocel FRC

Bin-ageing time, hours	Apparent hardness, IRHD	Young's modulus, MPa	Mean
0	37	4.5 3.9 4.0	4.1
0.5	39	5.0 4.7 4.9	4.9
1	46	4.1 4.4 4.0	4.2
2	48	4.7 5.0 4.6	4.8
4	48	4.9 5.6 5.3	5.3
6	50	5.1 5.6 4.8	5.2
24	57	6.0 6.5 5.5	6.0
48	60	8.7 9.5 9.4	9.2
72	63	8.0 9.2 broke	8.6
144	64	9.0 10.8 10.5	10.1
216	66	8.4 7.8 8.4	8.2
336	70	9.1 9.5 ND	9.3

ND not determined

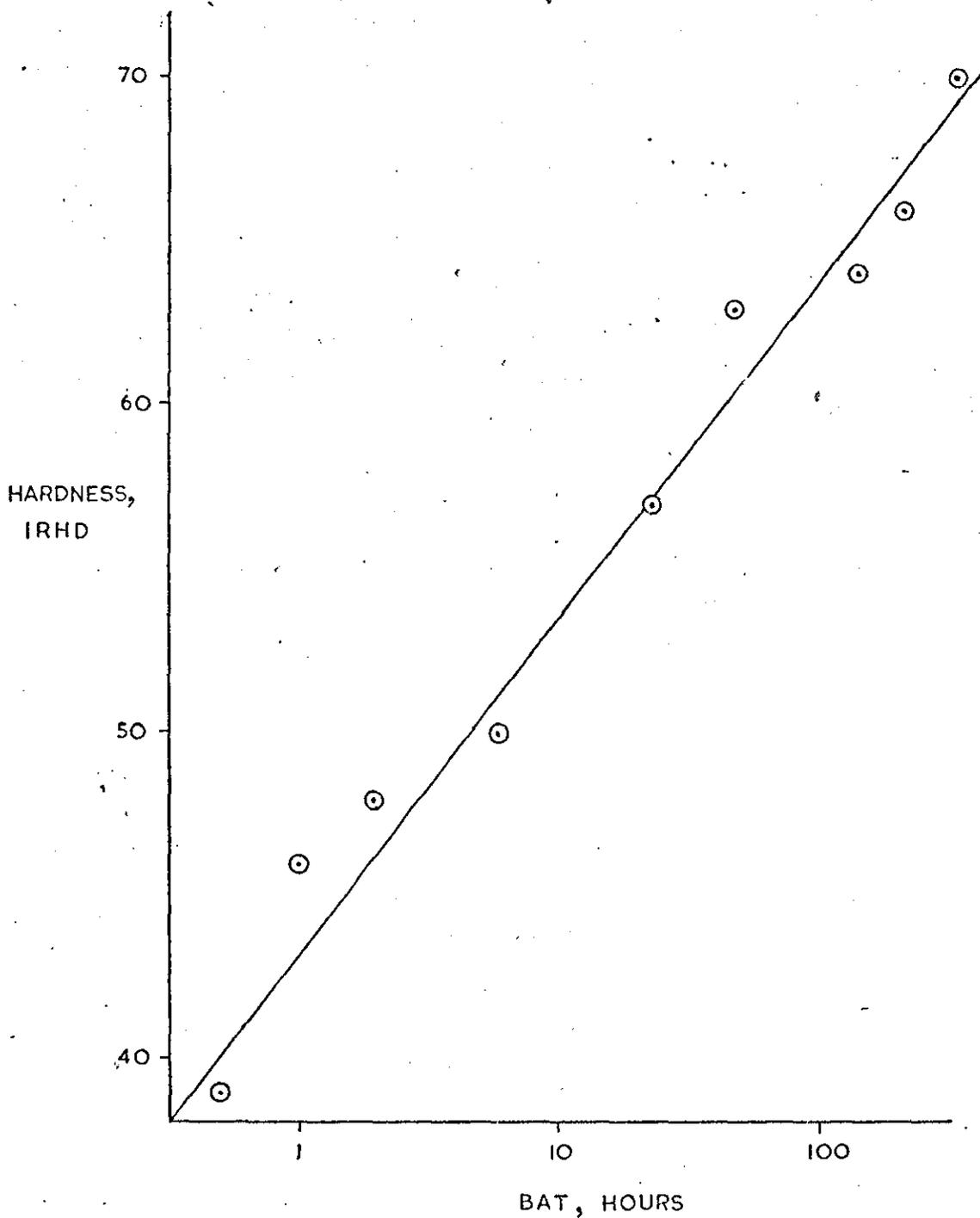


Figure 5.2 Relationship between apparent hardness and bin-aging time (BAT) for unvulcanised E302 containing 30 phr of Santocel FRC

The lower molecular weight batch of E302 which gave a higher rate of increase of breakdown time (Figure 3.3) also gave a higher rate of increase of Young's modulus on bin-ageing.

Fillers are known to produce three-dimensional structures and could contribute to the thixotropy of silicone rubber-silica mixes as, for example, observed with E302 containing 30 phr of Aerosil 300 (Figure 5.3). Remilling after initial attainment of the equilibrium Young's modulus caused a decrease which was partially recovered on further bin-ageing; following several such cycles the Young's modulus stabilised at a very low value.

Additional working during mixing, beyond the 30 minutes required to disperse the filler decreased the initial Young's modulus and apparent hardness of E303 containing 32 phr of Aerosil 300 but did not significantly affect the equilibrium values; (Table 5.2).

The rate of change of properties on bin-ageing seems low for simple re-formation of filler-filler structures while the permanent decrease of values would require extensive reduction of the molecular weight of matrix rubber if the effect was due solely to filler-filler structures. Taken together the results indicate that

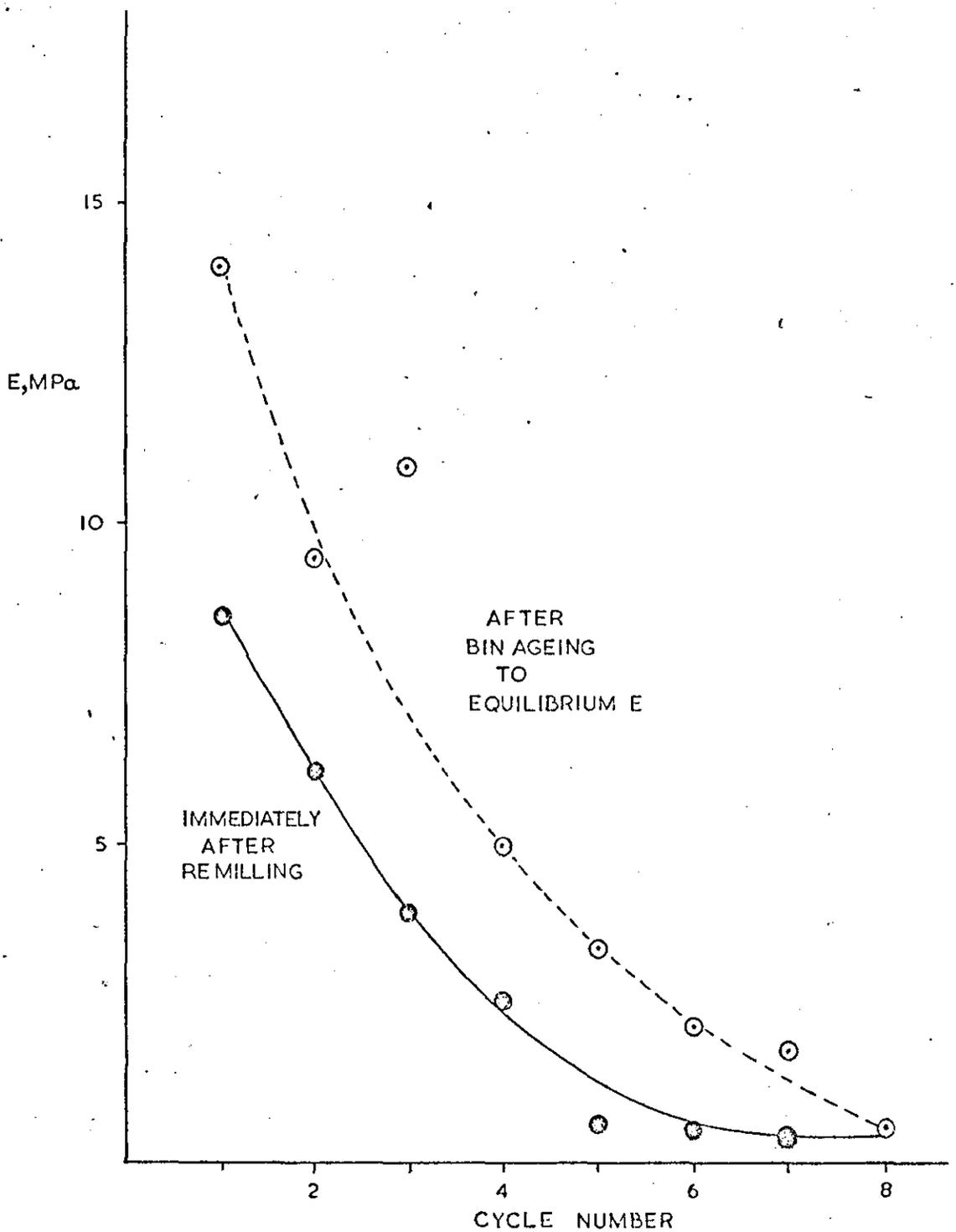


Figure 5.3 Effect of remilling on Young's modulus (E) of unvulcanised E302 containing 30 phr of Aerosil 300, after bin-ageing to equilibrium Young's modulus

Table 5.2 Effect of mixing time on the Young's modulus, MPa (and apparent hardness, IRHD) of E303 containing 32 phr of Aerosil 300

Bin-ageing time, days	Total mixing time, min	30	42	60
	0		5.1 (34)	4.7 (32)
3		5.5 (36)	4.9 (33)	4.0 (19)
16		10.1 (46)	10.2 (47)	8.3 (38)
70		ND (53)	10.1 (52)	9.7 (54)
127		ND (60)	ND (54)	ND (56)
177		ND (61)	ND (56)	ND (59)

ND not determined

Young's modulus and hardness, and their changes on bin-ageing and/or remilling, are not solely due to changes in the amount of filler-filler structure.

The increase in Young's modulus and apparent hardness on bin-ageing, and the partially reversible decrease on remilling, were confirmed for several silicone rubbers including E303 containing 32 phr of Aerosil 300 (Table 5.3).

Elasticity was also conferred by other fillers but not so effectively, as shown by Young's modulus (Table 5.4) particularly when allowance was made for the high concentrations used. Differences between fillers were reduced by vulcanisation but Aerosil 300 was unique in that vulcanisation had little effect on Young's modulus (Table 5.4).

Some of these fillers were compared at constant filler concentration (30 phr) in vulcanised E302 (Table 5.5) and the values indicated other than a simple dependence on particle size even when the surface treated filler (EP 154) was excluded: this was further demonstrated by increasing the range of fillers (Table 5.6).

The effect of Aerosil 300 concentration on the Young's modulus of E302, immediately after vulcanisation and on attainment of an equilibrium value on prolonged storage,

Table 5.3 Effect of remilling on the Young's modulus and apparent hardness of E303 containing 32 phr of Aerosil 300

Property	Young's modulus, MPa		Apparent hardness IRHD	
	before	after	before	after
Bin-ageing time, weeks (1 day)	6.0	5.7	48	41
1	6.1	5.0	59	31
2	7.0	3.2	62	39
3	4.7	3.9	54	34
4	4.6	ND	58	<28
8	14.5	6.5	66	42
9	11.4	6.6	58	<28
10	11.7	5.3	54	<28
11	6.5	1.3	45	<28
12	3.3	ND	32	<28
13	2.0	ND	<28	<28
14	0.3	ND	<28	<28
26	11.7	7.5	70	44
27	ND	ND	63	35
28	7.5	2.4	52	<28
29	3.9	0.6	39	<28
30	1.1	ND	29	<28
31	ND	ND	<28	<28

Values between pairs of horizontal lines were obtained successively on the same test portions.

ND not determined

Table 5.4 Effect of filler type and vulcanisation on the Young's modulus of E302

Filler		Young's modulus, MPa	
Type	Concentration, phr	Unvulcanised	Vulcanised
Ballotini	350	< 0.1	8.4
Minusil	200	< 0.1	4.5
Celite Superfloss	120	< 0.1	8.2
EP 154	56	1.1	5.0
MT black	298	3.4	35.8
SAF black	75	1.1	6.8
Aerosil 300	40	15.0	13.2

Table 5.5 Effect of filler and storage time on the Young's modulus, MPa (and apparent hardness, IRHD) of vulcanised E302

Filler	Aerosil 300	Aerosil 200	Santocel FRC	Celite Superfloss	Minusil	EP 154
Particle size, nm	12	25	30	3,000	10,000	12
Storage time, days						
0	5.8(62)	5.0(54)	8.8(53)	1.4(33)	0.7(28)	2.0(47)
3	7.2(71)	5.2(66)	10.0(70)	1.4(35)	0.8(28)	2.0(46)
7	ND (75)	ND (64)	9.2(74)	ND (36)	ND (29)	ND (49)
10	ND (78)	ND (69)	8.4(70)	ND (37)	ND (28)	ND (48)
14	7.4 (77)	7.0(72)	8.0(74)	1.4(36)	0.8(28)	2.5(50)
21	ND (80)	ND (75)	ND (80)	ND (37)	ND (28)	ND (47)
48	8.2(80)	7.0(76)	10.0(80)	1.4(37)	0.8(28)	2.4(48)

ND not determined

Table 5.6 Effect of 32 phr of further fillers on the Young's modulus and apparent hardness of E302 immediately after vulcanisation

Filler	Description	Particle size, nm	Specific surface area, m <sup>2</sup> /g	Young's modulus, MPa	Apparent hardness, IRHD
Hi-Sil 233	Hydrated silica	22	150	2.1	52
T 5306	Melamine-formaldehyde	35	140-150	0.2	<28
Fransil 251	Anhydrous silica	40	-	0.8	29
VT 4	Urea-formaldehyde	45	55-75	3.2	48
Aerosil 200*	Fume silica	25	200	See Table 5.5	
Philblack E*	SAF black	20-25	130	1.2	33
Thermax**	MT black	300-500	8	0.9	34

\* 30 phr

\*\* 50 phr

was compared (Figure 5.4) with that predicted by the Guth-Gold equation (Section 11.2). Similar comparison was made for a range of fillers (Figure 5.5).

On the other hand the apparent hardness of vulcanised E302 tended to be proportional to the filler volume concentration, particularly in the presence of EP 154 (Figure 5.6).

The crosslink density of silicone rubber vulcanisates is usually increased by an increase in the peroxide concentration e.g. the Young's modulus of E302 increased from 0.08 to 0.6 MPa when the peroxide concentration was increased from 0.15 to 2.5 phr. However, in the presence of 32 phr of Aerosil 300, Young's modulus decreased as the peroxide concentration was increased from 0.5 to 2.5 phr but, nevertheless, there was an increase in apparent hardness (Table 5.7).

Low values of Young's modulus, similar to those obtained by remilling after bin-ageing at room temperature (Figure 5.3 and Table 5.3), were also obtained:-

- a) by remilling after heat treatment
- b) with normal filler in low molecular weight polymer (MS 200)
- c) with surface treated filler (EP 154) in normal polymer.

Thus, typical values obtained with 30/32 phr of filler (Table 5.8) indicated similar final structures

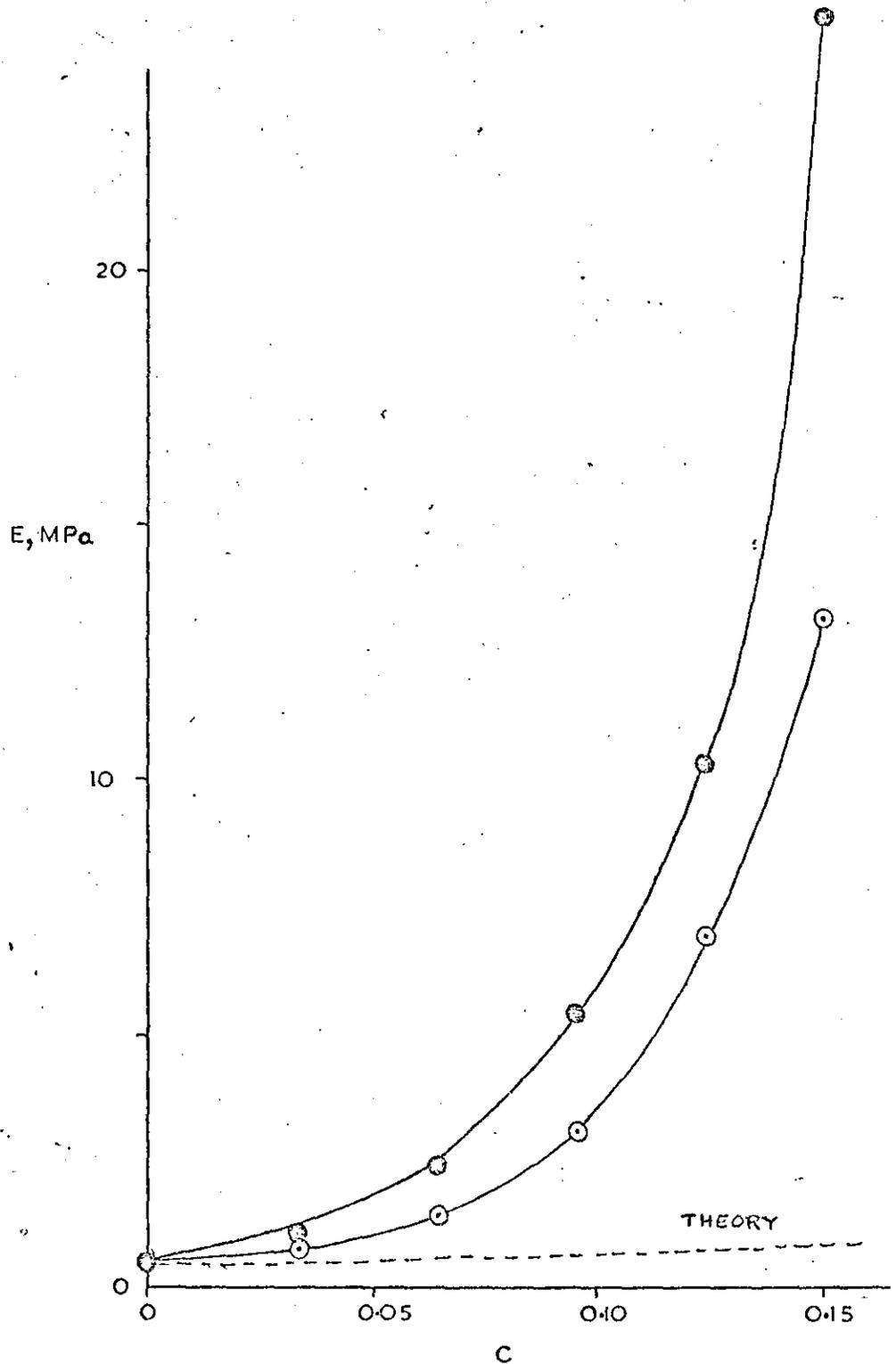


Figure 5.4 Dependence of Young's modulus (E) of vulcanised E302 on the volume concentration (c) of Aerosil 300 in comparison with values predicted by

$$E = E_0 (1 + 2.5c + 14.1c^2) \dots \dots (2)$$

(Storage time ○ nil ● 57 days)

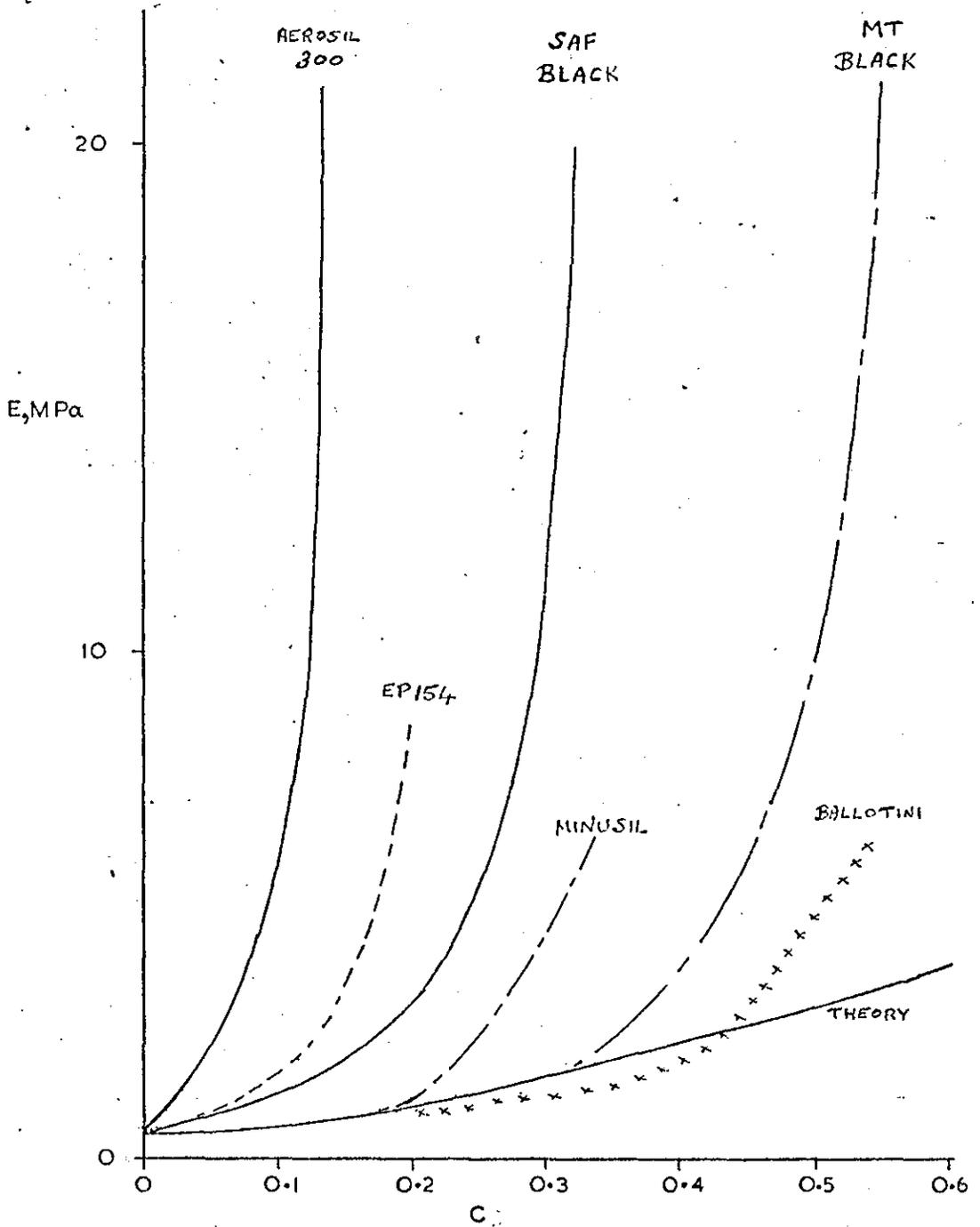


Figure 5.5 Dependence of Young's modulus (E) of vulcanised E302 on the volume concentration (c) of various fillers, in comparison with values predicted by equation (2)

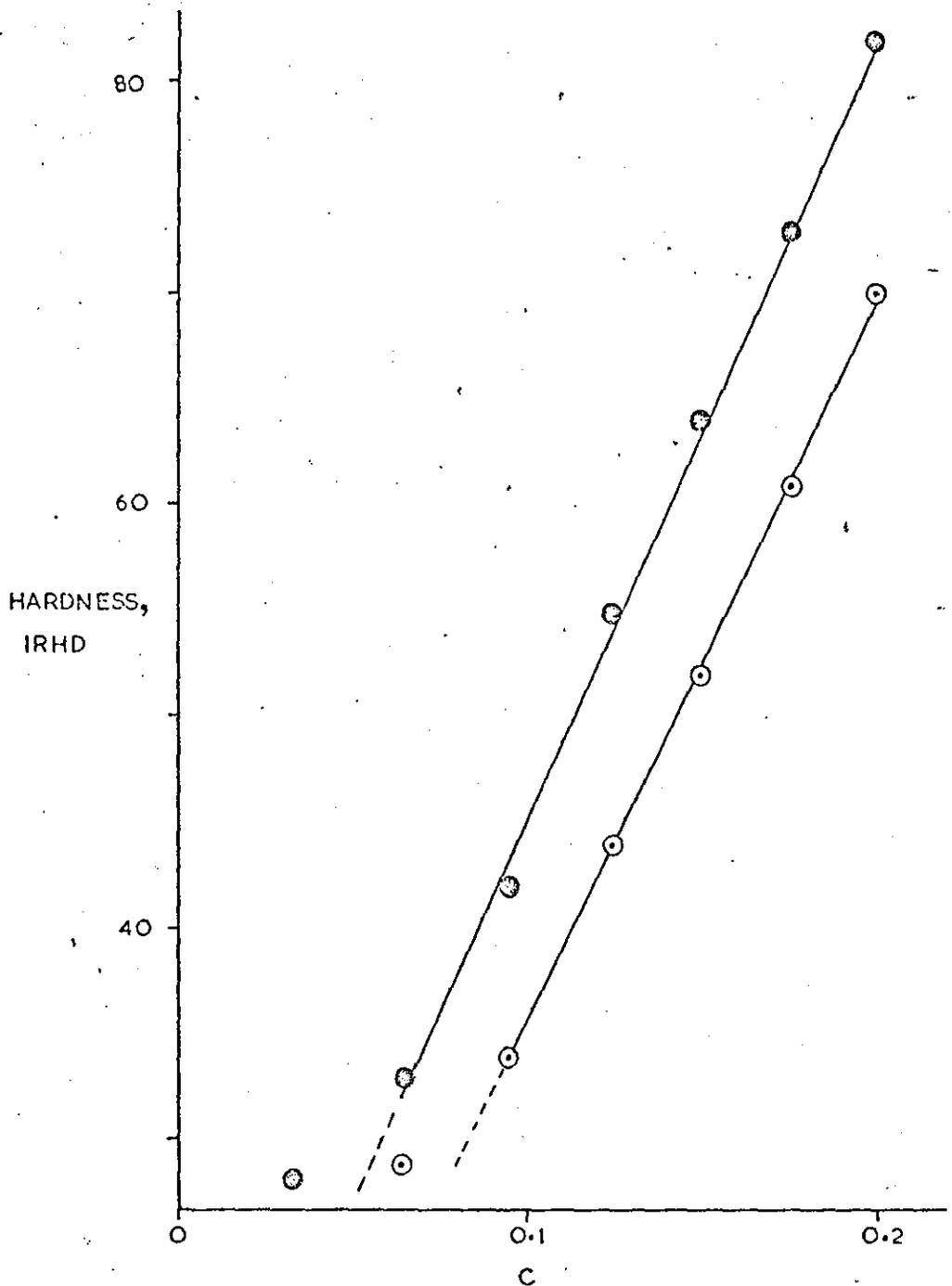


Figure 5.6 Relationship between apparent hardness of vulcanised E302 and the volume concentration (c) of EP 154 (Storage time  $\circ$  nil  $\bullet$  1 month)

Table 5.7 Effect of peroxide concentration and storage time on the Young's modulus, MPa (and apparent hardness, IRHD) of Vulcanised E302\*

Storage time, weeks	Peroxide concentration, phr				
	0.5	1.0	1.5	2.0	2.5
0	7.4(66)	7.1(68)	6.0(69)	6.1(70)	6.0(72)
1	9.1(75)	9.2(77)	7.8(77)	7.6(78)	6.6(78)
2	9.3(78)	8.3(80)	7.5(81)	7.2(81)	7.2(82)
3	10.9(78)	10.1(79)	9.1(80)	9.2(81)	9.2(81)
7	12.7(81)	12.5(81)	10.9(81)	11.1(81)	10.8(80)
10	12.9(81)	13.3(83)	12.0(83)	11.6(83)	10.8(84)

Table 5.8 Various methods of obtaining low values of Young's modulus and apparent hardness in vulcanised polysiloxanes

Filler*	Polymer	Young's modulus, MPa	Apparent hardness, IRHD
Aerosil 300	MS 200	1.6	39
Aerosil 300 (30 phr)	E302 successively remilled etc. (Figure 5.3)	1.8	47
Aerosil 300	E302 remilled after 4 hours at 250°C	2.0	54
EP 154	E302	2.0	47

\* 32 phr of Aerosil 300 or 30 phr of EP 154

in spite of the large differences there must have been in initial structures. It is proposed that the final structure was due to filler made largely inactive by pretreatment in the case of EP 154 or by attachment of adsorbed rubber in the other cases. It is further proposed that some interparticular rubber provided weak structures in the unvulcanised state, except in the case of MS 200, and that these two forms plus matrix rubber were joined by peroxide induced crosslinks in the vulcanised state.

#### 5.1.2 Organic rubbers

Organic rubbers also exhibited Hookean behaviour at low strains so it was possible, for comparison, to determine the effect of several fillers on the Young's modulus of natural rubber and nitrile rubber; in the unvulcanised state; after remilling and addition of peroxide; and in the vulcanised state. There were no significant changes on bin-ageing or storage and mean values showed a considerable decrease in the order Aerosil 300, Hi-Sil 233, SAF black, MT black even though the first three had little difference in particle size (Tables 5.9 and 5.10): the high Young's modulus obtained with Aerosil 300, and the lack of direct correlation between Young's modulus and filler particle size were thus shown not to be unique to silicone rubber.

Table 5.9 Effect of fillers, remilling and vulcanisation on the Young's modulus, MPa (E) and apparent hardness, IRHD (H) of natural rubber

Filler*	Unvulcanised		Remilled		Vulcanised	
	E	H	E	H	E	H
Nil	ND	ND	ND	ND	0.9	34
MT black	0.4	<28	0.2	<28	2.4	61
SAF black	0.7	<28	0.4	<28	2.3	61
Hi-Sil 233	4.2	62	3.3	45	15.3	88
Aerosil 300	14.2	79	9.1	74	22.5	93

\* 100 phr of MT black or 50 phr of other fillers

ND not determined

Table 5.10 Effect of fillers and vulcanisation on the Young's modulus, MPa (E) and apparent hardness, IRHD (H) of nitrile rubber

Filler*	Unvulcanised		Vulcanised	
	E	H	E	H
Nil	0.8	29	1.2	44
MT black	3.2	55	5.8	72
SAF black	3.7	58	4.9	70
Hi-Sil 233	7.5	75	17.7	85
Aerosil 300	17.0	86	22.8	92

\* 100 phr of MT black or 50 phr of other fillers

ND not determined

## 5.2 YIELD STRESS

Plotting of the first yield stress values obtained for unvulcanised E302 against the square root of bin-ageing time (Figure 5.7) gave straight lines with slopes whose logarithm was proportional to the concentration (phr) of Aerosil 300 (Figure 5.8).

In later determinations yield stress was proportional to bin-ageing time and the rate of change was much greater: stress was greater for Aerosil 300 than for Aerosil 200 (Figure 5.9). With EP 154 values were much lower and after 10 weeks bin-ageing, had only attained approximately 0.04 MPa.

Yield stress thus appears to be similar to Young's modulus in revealing reinforcement, probably because it arises from the initial failure of the structures which govern Young's modulus.

## 5.3 STRESS AT HIGHER EXTENSION

### 5.3.1 Silicone rubbers

Uncured E302 containing 40 phr of Aerosil 300 was found to be extremely weak; the highest value of tensile strength (Table 5.11) was only half that of vulcanised silicone gum (Table 1.1). Nevertheless values did increase on bin-ageing, as did particularly the elongation at break. This mix was crepe-hardened between 1 and 2 days without any apparent change in the trend.

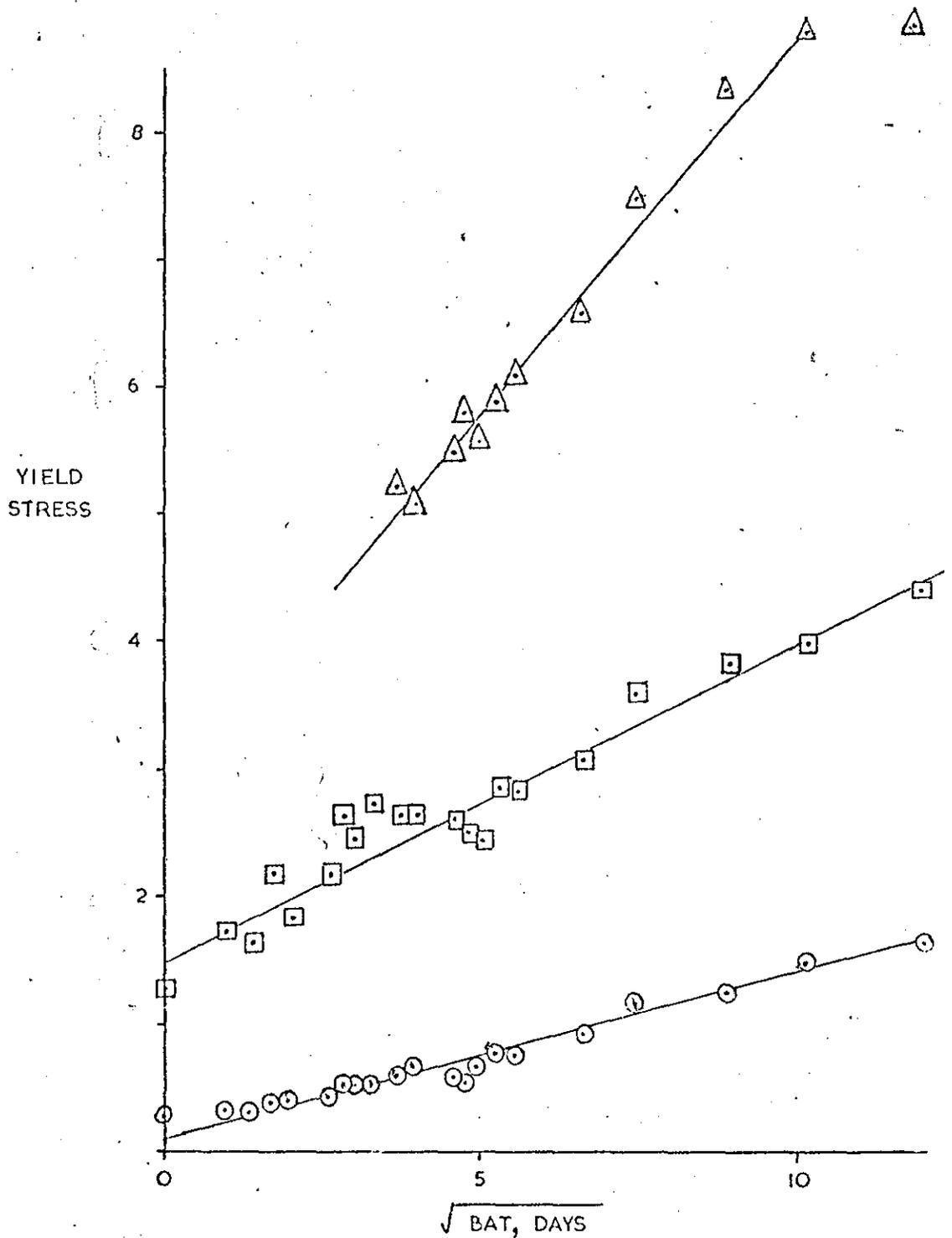


Figure 5.7 Relationship between yield stress (N/test-piece) of unvulcanised E302 and the square root of bin-ageing time (BAT) (Aerosil 300 concentration  
 ⊙ 16 phr    □ 24 phr    △ 32 phr)

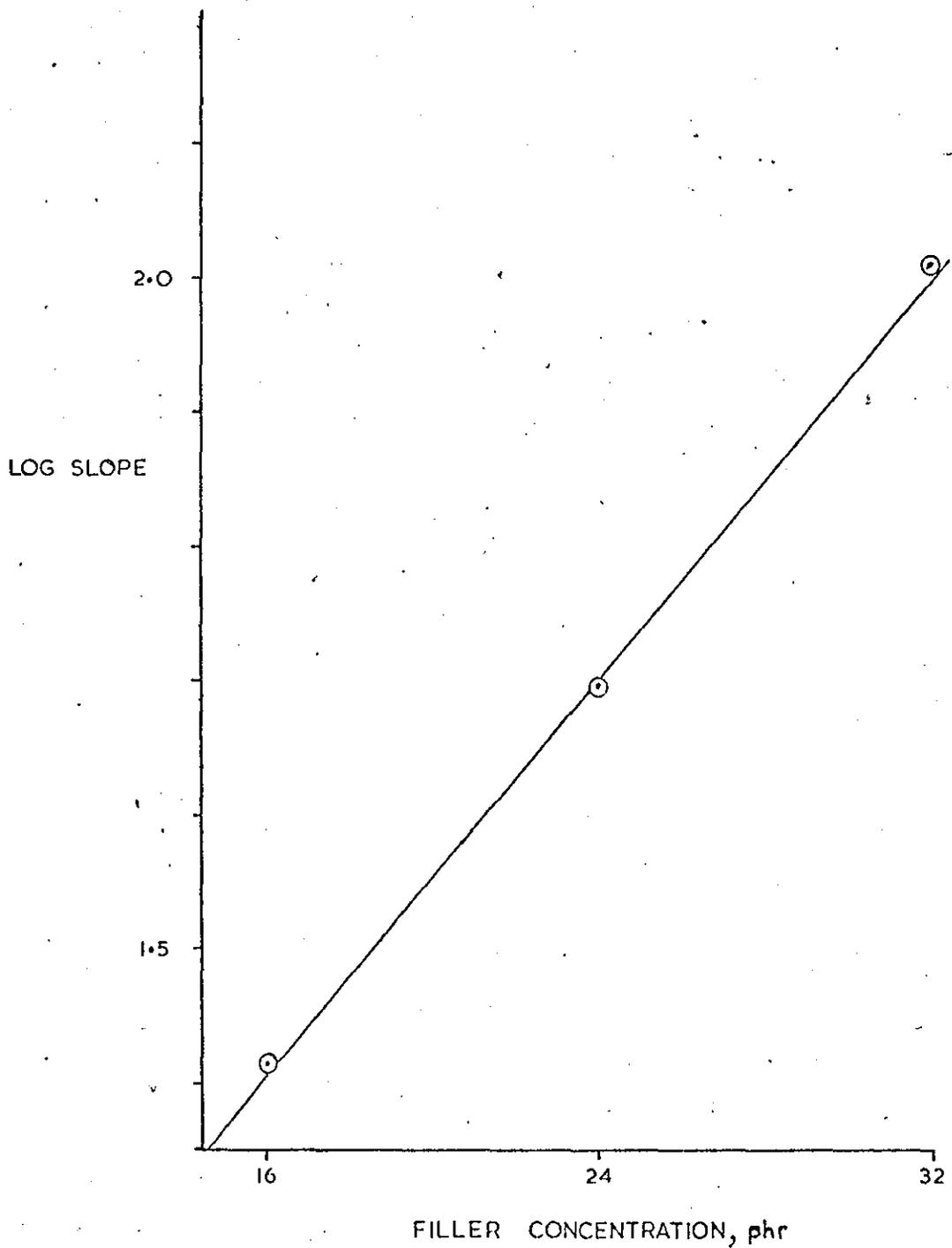


Figure 5.8 Relationship between logarithm of slopes (arbitrary units) of Figure 5.7 and concentration of Aerosil 300

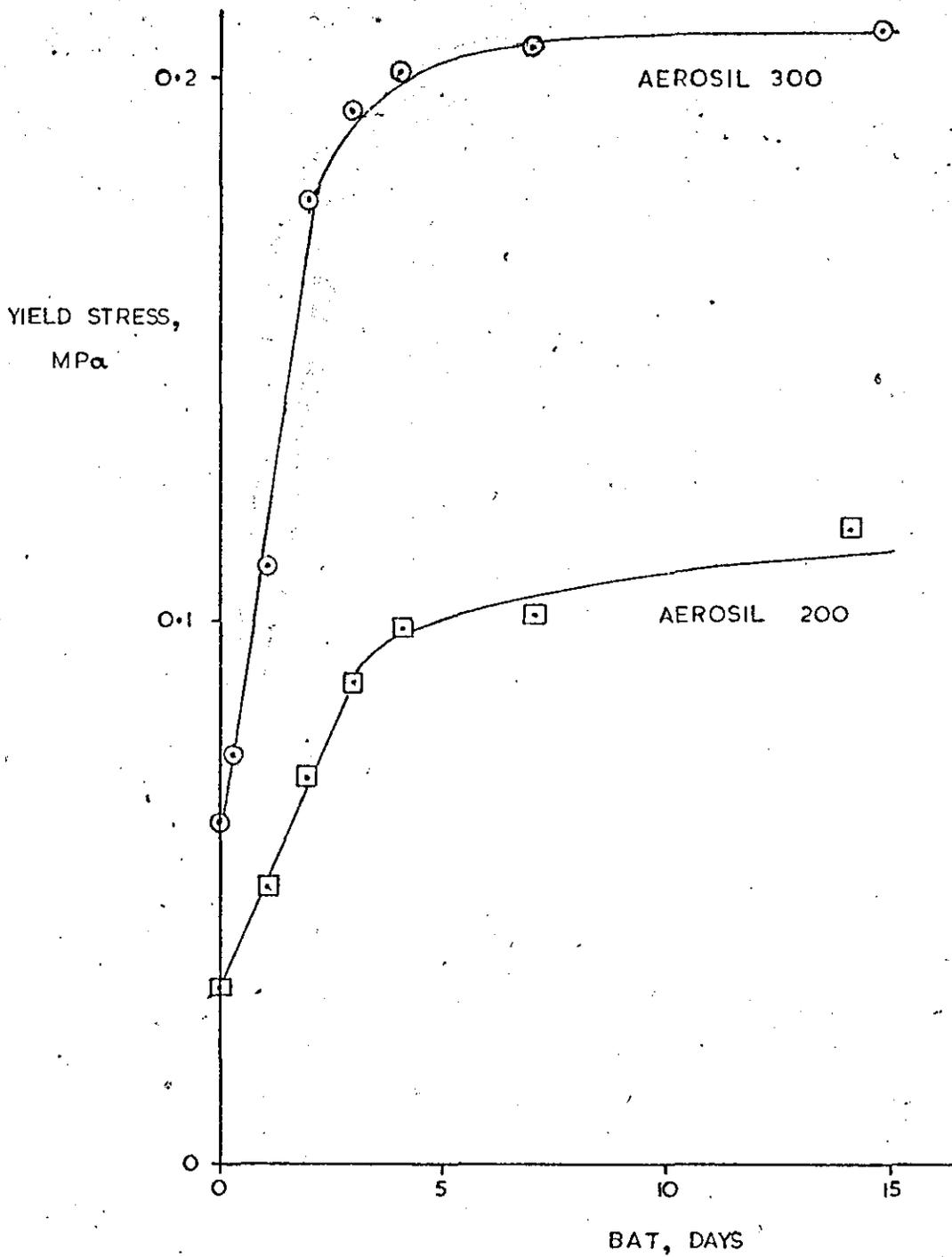


Figure 5.9 Effect of filler type on the relationship between yield stress and bin-ageing time (BAT) for unvulcanised E303

Table 5.11 The effect of bin-ageing on the tensile properties of E302 containing 40 phr of Aerosil 300

Bin-ageing time, days	Stress at 150% extension, MPa	Tensile strength, MPa	Elongation at break, %
1	-	0.11	10
2	-	0.10	10
3	-	0.12	10
7	0.11	0.15	310
10	0.11	0.15	300
14	0.12	0.16	550
16	0.13	0.14	224
18	0.13	0.15	420
22	0.13	0.15	420

The increase in elongation at break between 3 and 7 days was not due to this cause as was established with further non crepe-hardened mixes which similarly showed a large increase after a few days bin-ageing. With only 32 phr of Aerosil 300 the tensile strength increased on bin-ageing from 0.05 to 2.0 MPa in 128 days.

Enhancement of Young's modulus, stresses at various strains, and tensile strength by inclusion of Aerosil 300 in E303 vulcanisates, was compared with that expected theoretically (Figure 5.10).

Although Young's modulus was the property most enhanced by high filler concentrations, the others were still well in excess of the theoretical values and showed the much greater effect of the peroxide induced crosslinks at higher strains when compared with the values in Table 5.11 where tensile strength was only half that of a gum vulcanisate (Table 1.1).

### 5.3.2 Natural rubber

Stress at various strains and at break of vulcanised natural rubber containing Aerosil 300, determined on single dumb-bells, not surprisingly showed considerable scatter but there was no significant evidence of any dependence on storage time. The median values were therefore used to calculate stress enhancement ratios as in Section 5.3.1; these (Figure 5.11) were

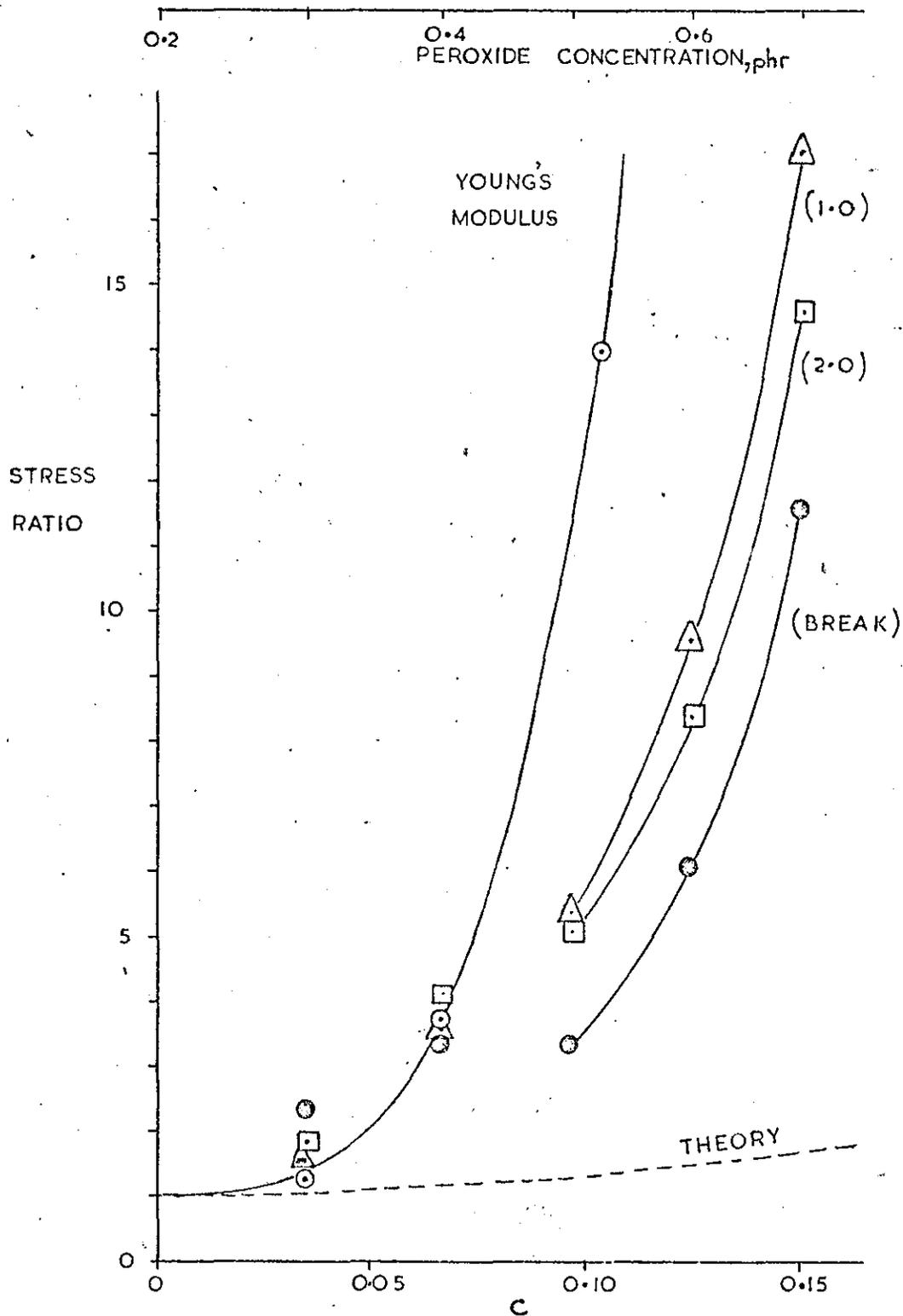


Figure 5.10 Dependence of stress (filled)/stress (unfilled) on the volume concentration (c) of Aerosil 300 in vulcanised E303 at various strains, in comparison with values predicted by equation (2)

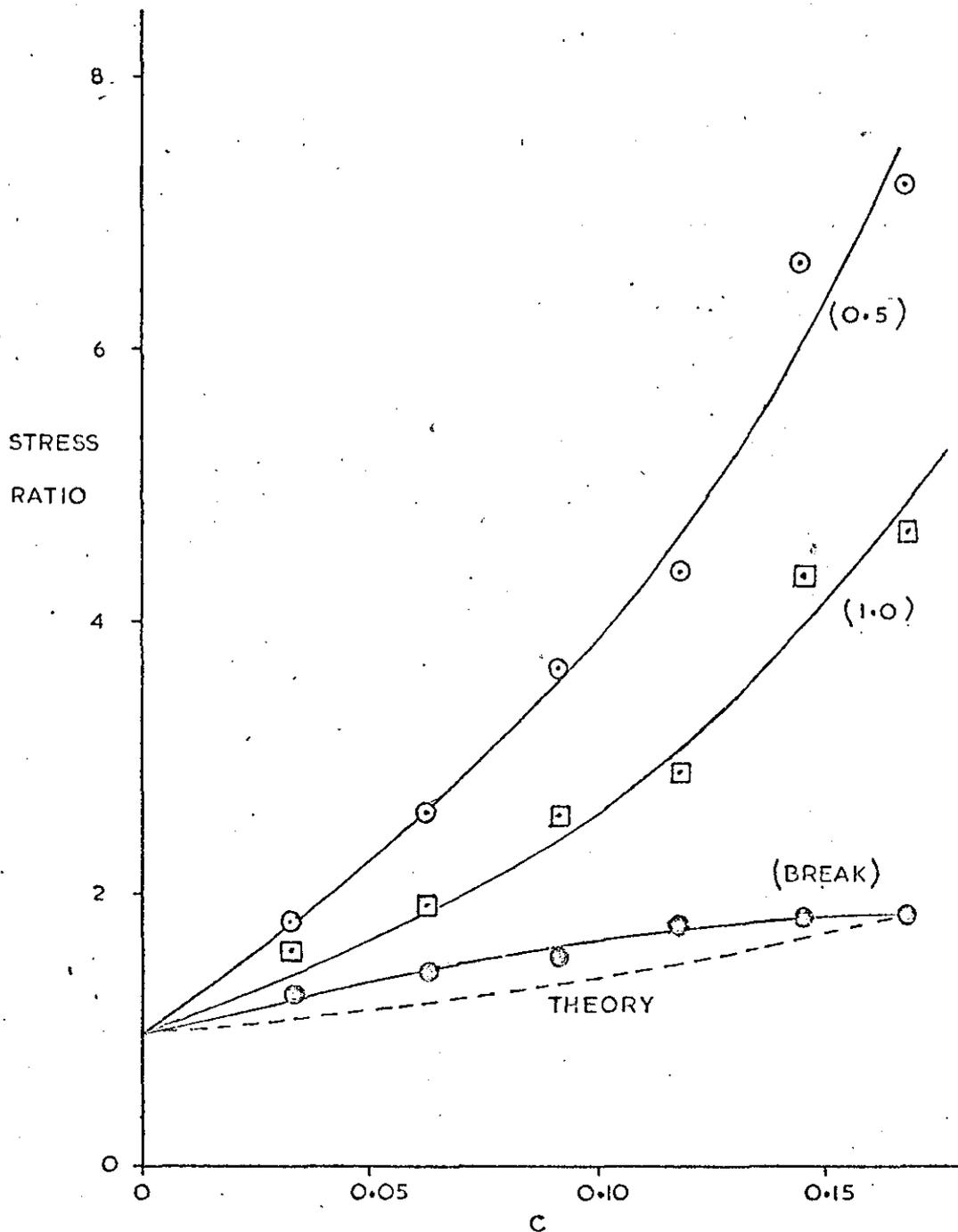


Figure 5.11 Dependence of stress (filled)/stress (unfilled) on the volume concentration ( $c$ ) of Aerosil 300 in vulcanised natural rubber at various strains, in comparison with values predicted by equation (2)

less than those for silicone rubber but nevertheless still well in excess of theoretical values, apart from tensile strength.

A different result was obtained when actual stresses of the two polymers (containing 40 phr of Aerosil 300) were compared: the stress of natural rubber was less than twice as high at a strain of 0.5 yet nearly six times as high at a strain of 5.0. Presented a different way, the ratio of the stress at a strain of 5.0 to the stress at a strain of 0.5 was 2.6 for silicone rubber but 8.1 for natural rubber. This effect is attributed to the tendency for natural rubber to crystallise at high extensions even in the presence of a fine particle silica.

#### 5.4 COMPRESSION MODULUS

Compression modulus of E303 vulcanisates has shown random variation on storage but mean values showed greater enhancement in the presence of filler than theoretical expectations (Figure 5.12) whether values were calculated from the slope of the initial linear region or from the more usual second linear region.

Mean values of sextuplicate determinations (second linear region) with a range of fillers were compared with values of Young's modulus determined immediately after moulding (Table 5.12). Although the relative

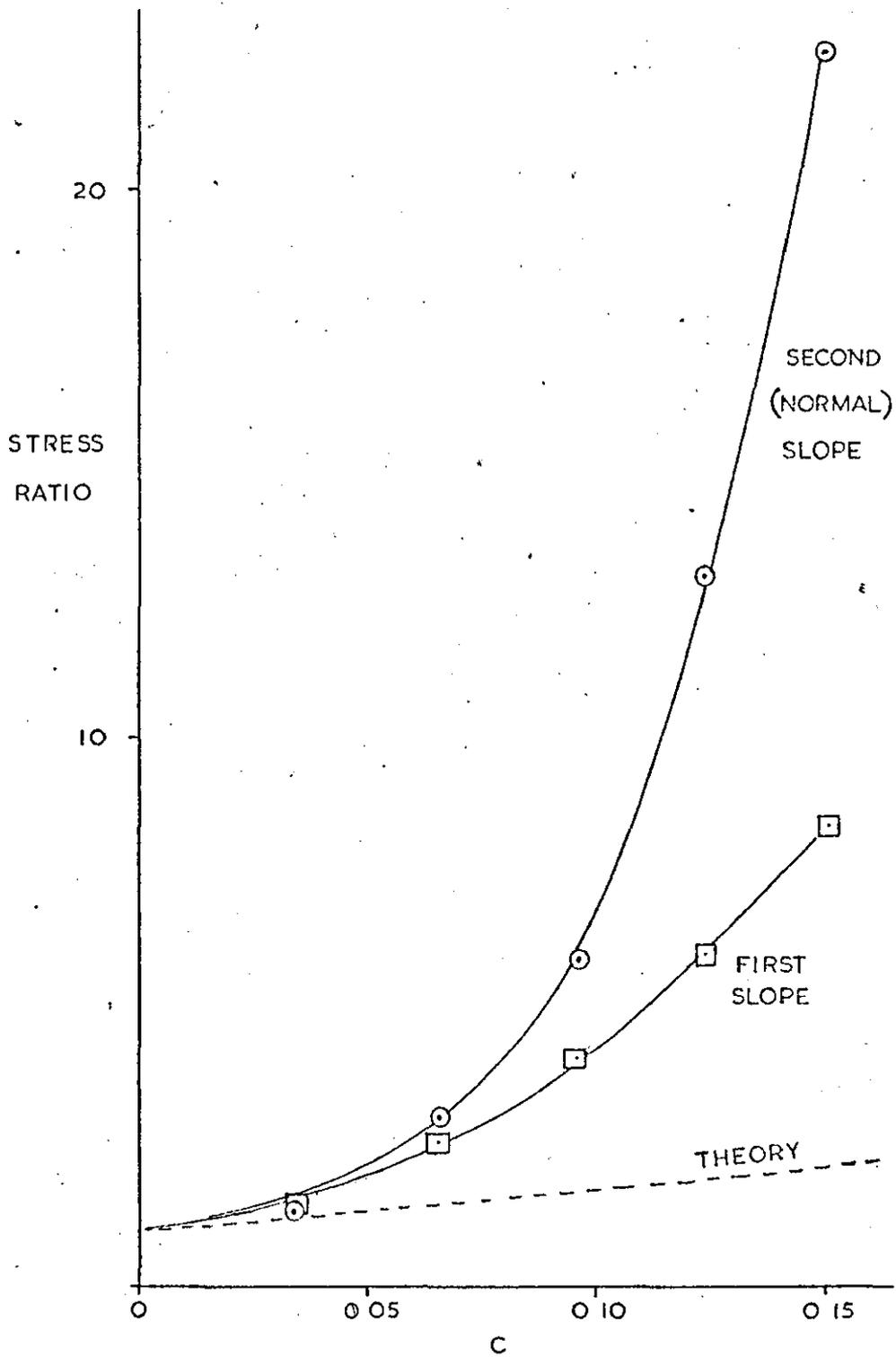


Figure 5.12 Dependence of compression modulus (filled)/compression modulus (unfilled) on the volume concentration (c) of Aerosil 300 in vulcanised E303, in comparison with values predicted by equation (2)

Table 5.12 Effect of filler type on the compression modulus of vulcanised E303

Filler (30 phr)	Compression modulus, MPa	$\frac{\text{Compression modulus}}{\text{Young's modulus}}$
Aerosil 300	4.28	0.74
Aerosil 200	3.30	0.66
Santocel FRC	4.09	0.47
Celite Superfloss	0.80	0.54
Minusil	0.62	0.89
EP 154	1.41	0.70

positions were, with the exception of Santocel FRC, the same the actual ratios were not constant; this may reflect slight differences between fillers in their comparative behaviour in the linear region of low extension and the usual linear region under compression (a linear region through the origin on compression was not detected in this series).

The enhancement with Santocel FRC appeared to be slightly abnormal (Figure 5.13) particularly in comparison with a more typical curve for EP 154; both curves were well above the theoretical curve however. On the other hand a similar curve for MT black gave good agreement with the theoretical curve at low concentrations and quite good agreement with the van der Poel curve at higher concentrations (Figure 5.14).

### 5.5 STRESS SOFTENING

Young's modulus was determined on natural rubber vulcanisates containing Aerosil 300 :

- a) as in Section 5.1.2
- b) after cycling to constant load until equilibrium appeared to have been achieved; maximum stress was approximately 5MPa; initial maximum strain varied from approximately 5.0 in the absence of filler to approximately 2.0 in the presence of 48 phr of filler
- c) after subsequent storage

Cycling reduced the Young's modulus but only to values still in excess of theoretical ones, and partial recovery occurred on the subsequent storage (Figure 5.15).

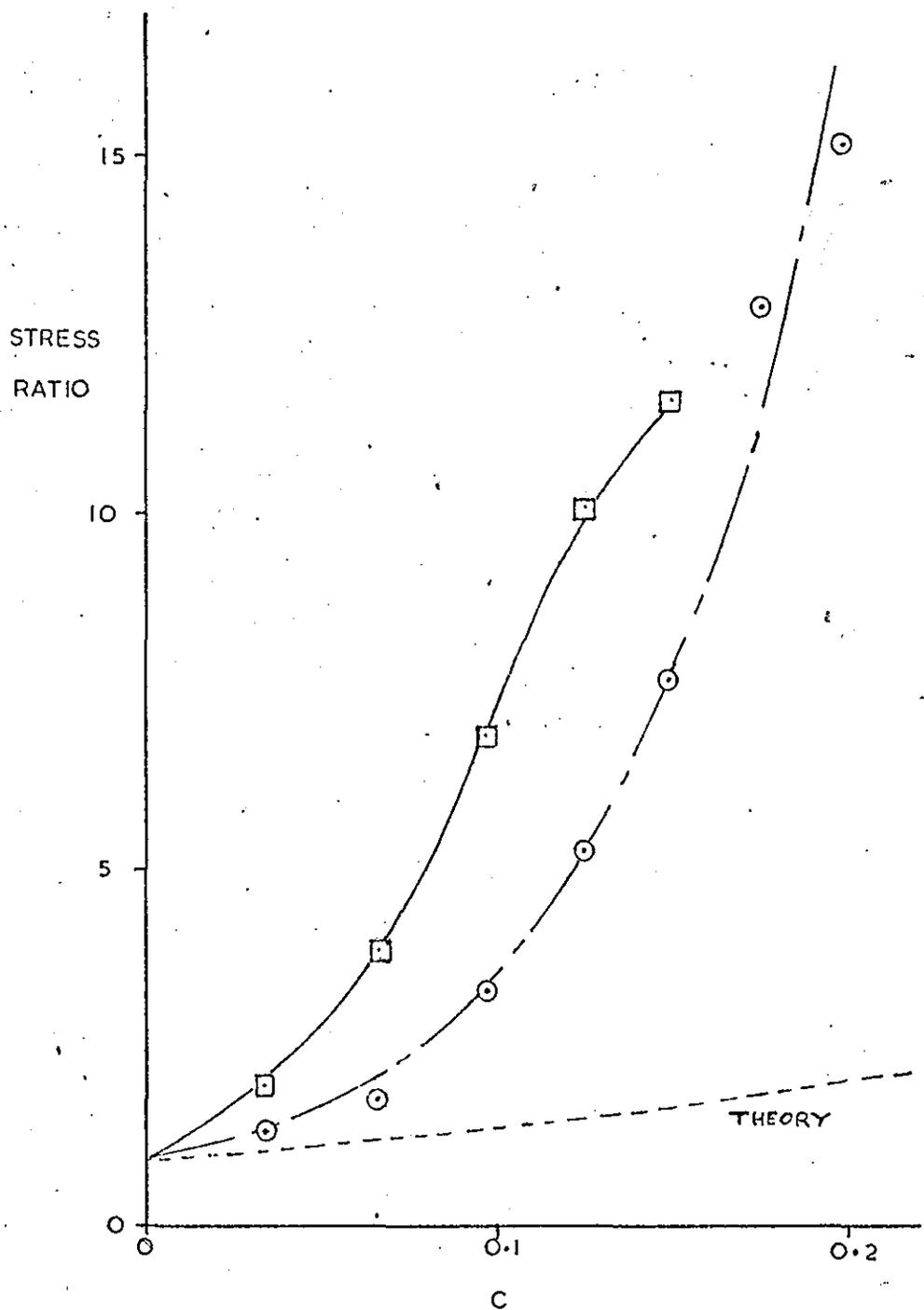


Figure 5.13 Dependence of compression modulus (filled)/compression modulus (unfilled) on the volume concentration ( $c$ ) of Santocel FRC  $\square$  in vulcanised E303, and of EP154  $\circ$  in vulcanised E302, in comparison with values predicted by equation (2)

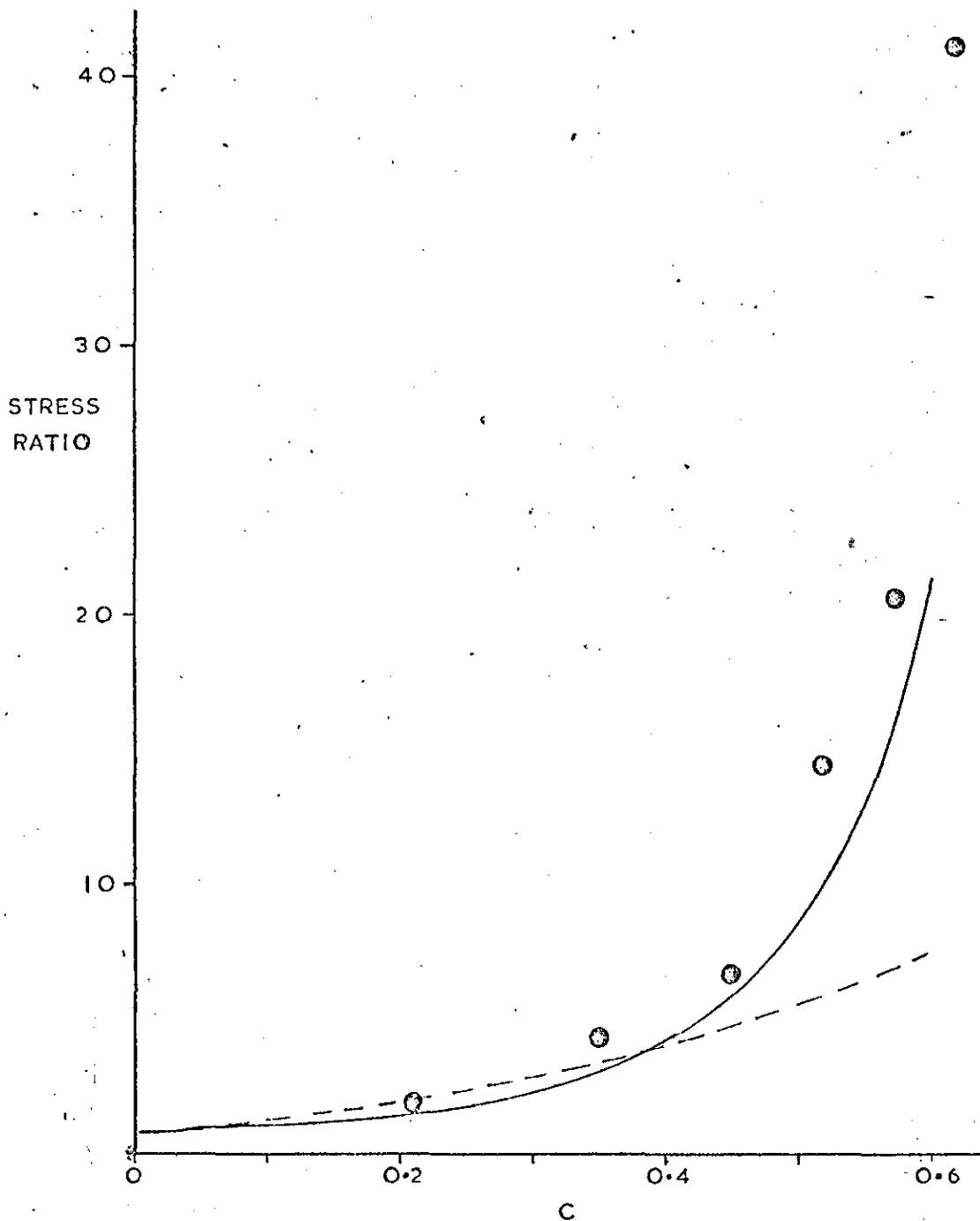


Figure 5.14 Dependence of compression modulus (filled)/compression modulus (unfilled) on the volume concentration (c) of MT black in vulcanised E302 in comparison with values predicted by equation (2) (-----) and van der Poel 1958 (—)

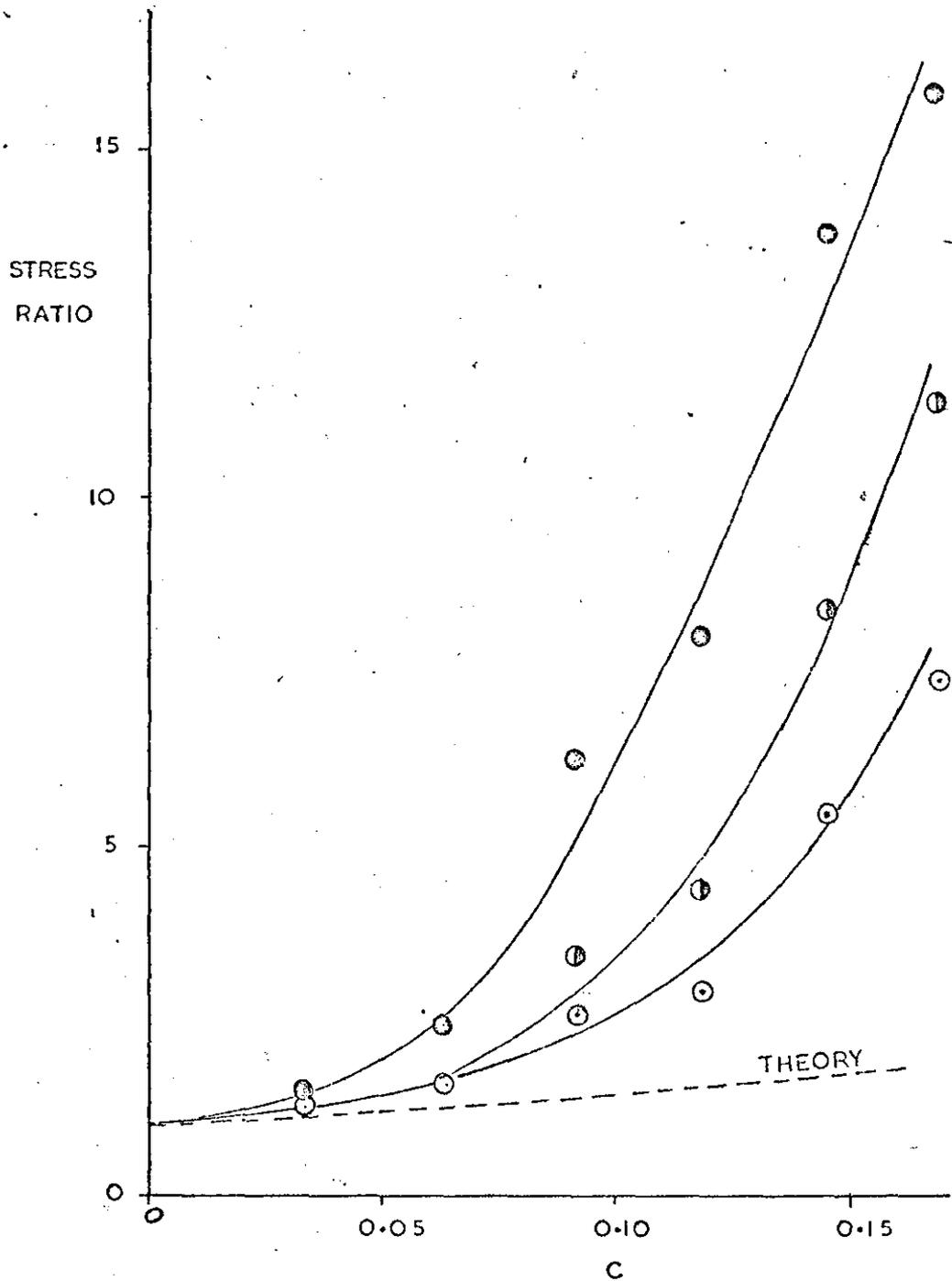


Figure 5.15 Dependence of Young's modulus (filled)/ Young's modulus (unfilled) on the volume concentration (c) of Aerosil 300 in vulcanised natural rubber, before  $\bullet$  and after "stress-softening"  $\circ$  and after storage for 1 week  $\circ$  , in comparison with values predicted by equation (2)

The low extensibility of silicone gum vulcanisates, and the very high modulus enhancement with silica, precluded similar measurements with conventionally cured vulcanisates. Preliminary work using very low peroxide concentrations indicated that only two cycles were required to reach the equilibrium softened state, far fewer than with natural rubber.

#### 5.6 CONCLUSIONS

The stress of vulcanisates at a given strain was generally in the order observed in organic rubber, dependent upon particle size and surface chemistry of the fillers but was greater, often much greater, than the stress calculated by application of the Guth-Gold relationship to the stress of the gum vulcanisate. This was particularly so with Aerosil 300 both in silicone rubber and in organic rubber, but only in the former was an increase observed on storage.

Similarly in unvulcanised mixes fillers, particularly Aerosil 300, increased stress at a given strain but only in silicone rubber did it increase on storage; another difference with silicone rubber is that the rubber itself has no measurable Young's modulus, as it flows even under its own weight, yet with Aerosil 300 it gave a Young's modulus in excess of that of natural rubber with the same concentration of Aerosil 300. Obviously Aerosil 300 produces some three-dimensional structure in silicone rubber and some of this might be filler-filler structure but this cannot account for

all the observed effect; particularly does it seem unlikely to account for the stiffening on storage of silicone rubber, as its low viscosity is less likely to impede the formation of filler-filler structure than is the high viscosity of organic rubbers where no change was observed on storage.

Some other interaction obviously occurs and it is proposed that this leads to the formation of adsorbed rubber and interparticular rubber, certainly in silicone rubber and possibly also in organic rubbers. The proportion of the two structures remains in doubt but it is not believed to be constant; rather is there believed to be a tendency for storage and remilling to increase the adsorbed rubber and reduce the interparticular rubber thus leading to a reduction of the Young's modulus and apparent hardness (Table 5.8).

Particularly intriguing are the discrepancies between Young's modulus and apparent hardness as the two properties should be directly related, at least for substantially elastic, isotropic materials (Davey and Payne 1964). Yet in Table 5.7 increase of peroxide concentration increased apparent hardness but decreased Young's modulus, indicating that the two properties differ in their response to changes in internal structure. Many of the values from this Chapter are plotted in Figure 5.16 and reveal that vulcanisate values are in fair agreement with that theoretical relationship.

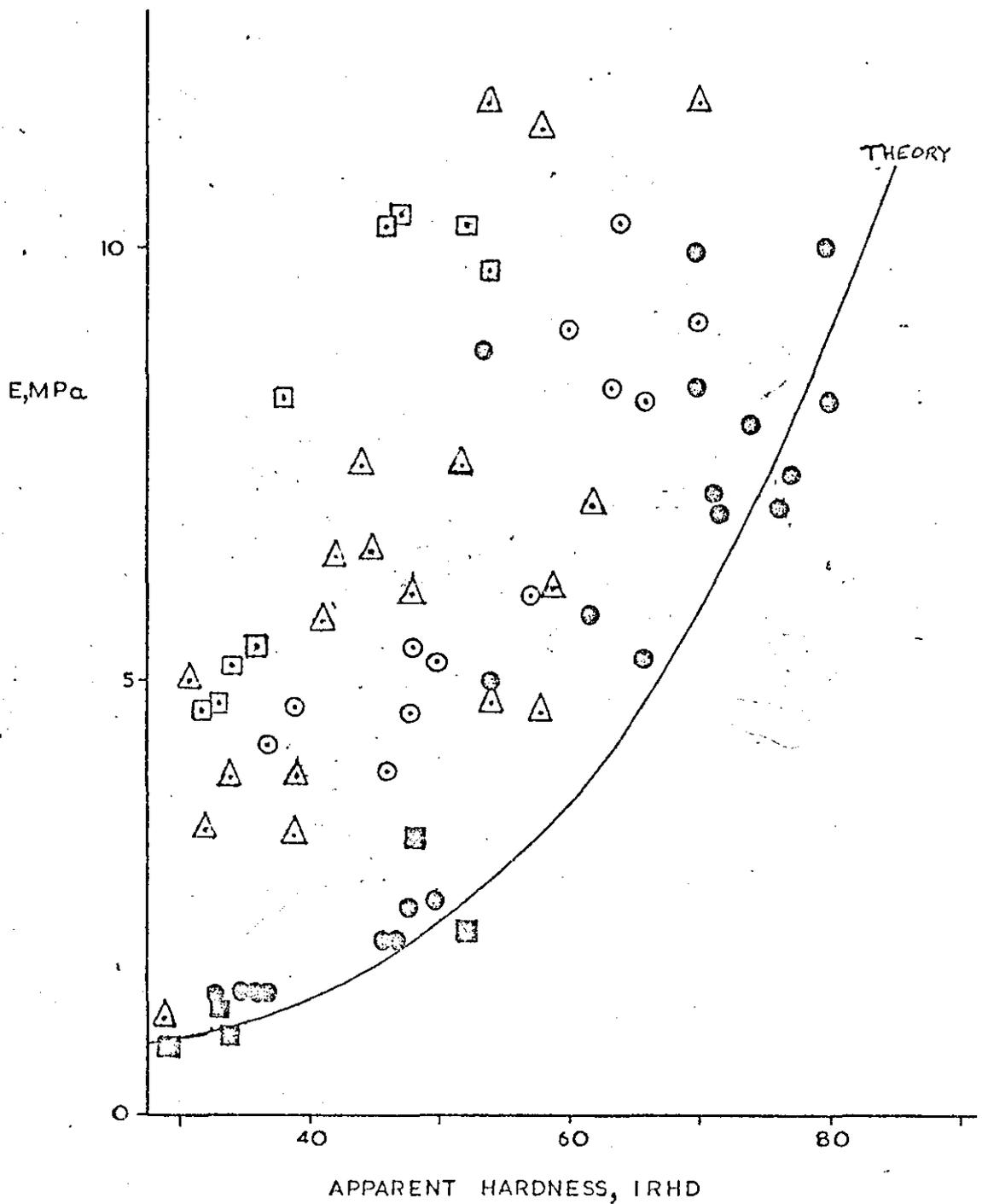


Figure 5.16 Relationship between Young's modulus (E) and apparent hardness (Data for unvulcanised mixes from Table 5.1 ○ , Table 5.2 □ and Table 5.3 △ ; for vulcanised mixes from Table 5.5 ● and Table 5.6 ■ )

Values of unvulcanised mixes reveal tremendous scatter but they are very significantly all on the same side of the theoretical curve, with abnormally high Young's modulus at given hardness. The values from Table 5.7 (omitting the 2 day values as anomalous) are given in Figure 5.17; they show successive displacements in the direction of the unvulcanised region to the vulcanised region with increase of peroxide concentration although none is in very good agreement with the theoretical curve.

Deviations from the normal Young's modulus-hardness relationship have been reported by Halliday and Southam (1971) for a number of vulcanisates so the effect is not peculiar to uncured mixes and/or silicone rubber. In all cases the differences may be due to internal structure and in the present work this is attributed to the unvulcanised mix having a more "open" structure, the space between filler particles being largely occupied by interparticular rubber in unvulcanised mixes and by crosslinked interparticular rubber in vulcanised mixes.

The initially low extensibility of unvulcanised silicone rubber mixes may be due to a delay in forming sufficient interparticular rubber but tensile strength remains low even when extensibility is high, implying failure by siloxane bond failure (as in a gum vulcanisate),

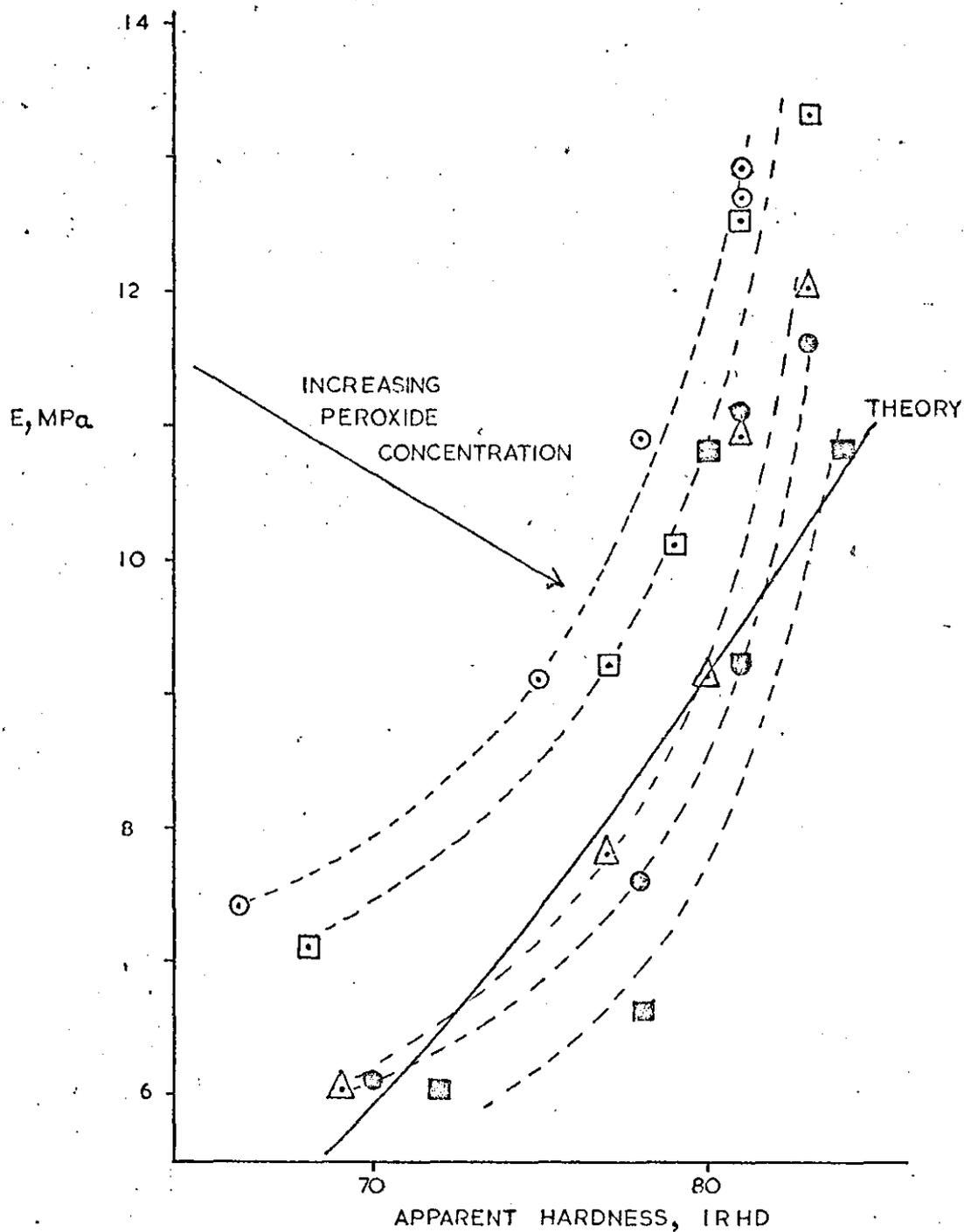


Figure 5.17 Effect of peroxide concentration on the relationship between Young's modulus (E) and apparent hardness (○ 0.5 phr ◻ 1.0 phr △ 1.5 phr ⊙ 2.0 phr ◼ 2.5 phr) (Data from Table 5.7)

presumably in interparticular rubber segments.

Introduction of peroxide induced crosslinks obviously has a different effect at high strains than at low strains. In the presence of filler, assuming that such crosslinks are formed between touching polymer chains, there could well be little effect on the low strain modulus of the proposed structures yet a very large effect on high strain modulus and failure properties.

## CHAPTER 6 HEAT OF MELTING

### 6.1 EFFECT OF FILLER CONCENTRATION

Successive measurements, generally in duplicate, were made on portions of E303 containing various concentrations of Aerosil 300 to determine the effect of filler concentration and bin-ageing time on the heat of melting (Figure 6.1). Fresh portions exhibited different heats of melting but they were still dependent on bin-ageing time. The measurements on the mix with 32 phr of filler commenced 92 days before the others.

Aerosil 300 clearly reduced the heat of melting of E303 but the effect was dependent on concentration and bin-ageing time; so too was the time to maximum reduction. Of the three concentrations 32 phr had the greatest effect, with lowest initial value, lowest minimum value and shortest time to that minimum.

Yagfarov, Ionkin and Gizatullina (1969) reported similar decreases in heat of melting of silicone rubber containing Aerosil but their minimum occurred at approximately 10 phr; however they did not report any consideration of bin-ageing.

### 6.2 EFFECT OF HEAT TREATMENT

It was found possible to accelerate the changes in the heat of melting of E303 containing 32 phr of Aerosil 300 either by varying the time at constant temperature (100°C)

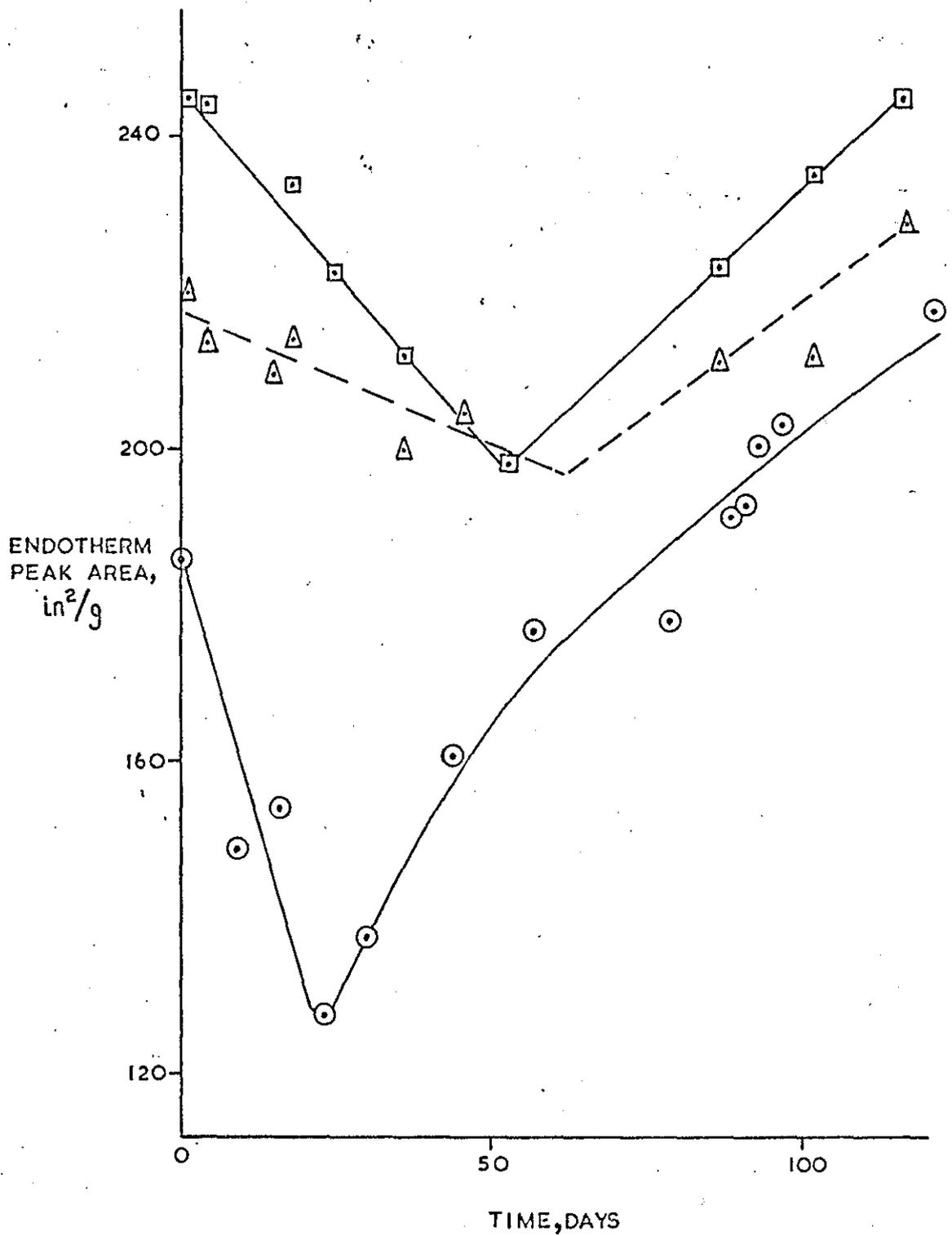


Figure 6.1 Effect of storage time and Aerosil 300 concentration on the heat of melting of E303

(  $\square$  40 phr    $\circ$  32 phr    $\triangle$  20 phr )

or by varying the temperature at constant time (24 hours) (Figure 6.2). For the former, measurements were made after the same total time and the balance of the time, at room temperature, was disregarded.

### 6.3 EFFECT OF FILLER TYPE

Heats of melting of 235-253 in<sup>2</sup>/g were obtained for E303 containing 32 phr of Minusil compared with a mean E303 value of 246 in<sup>2</sup>/g and thus revealing no significant effect: there was generally a pronounced shoulder on the low temperature side of the recorded peak.

Similar values were obtained for E303 containing 120 phr of Celite Superfloss after treatment for 24 hours at various temperatures: although these were within experimental error there was some slight indication of a minimum between room temperature and 40°C.

Some values were obtained on E303 containing 32 phr of Aerosil 200; these were fairly inconclusive except that the difference between samples stored for 24 hours at room temperature and 70°C was slightly less than the range in Figure 6.1 with 32 phr of Aerosil 300.

The variability introduced by heat treatment was even greater for E303 containing 32 phr of EP 154 (Figure 6.3); data almost appeared to be random variations but closer inspection revealed some order between 0 and 100°C for values obtained in the same session, but big differences

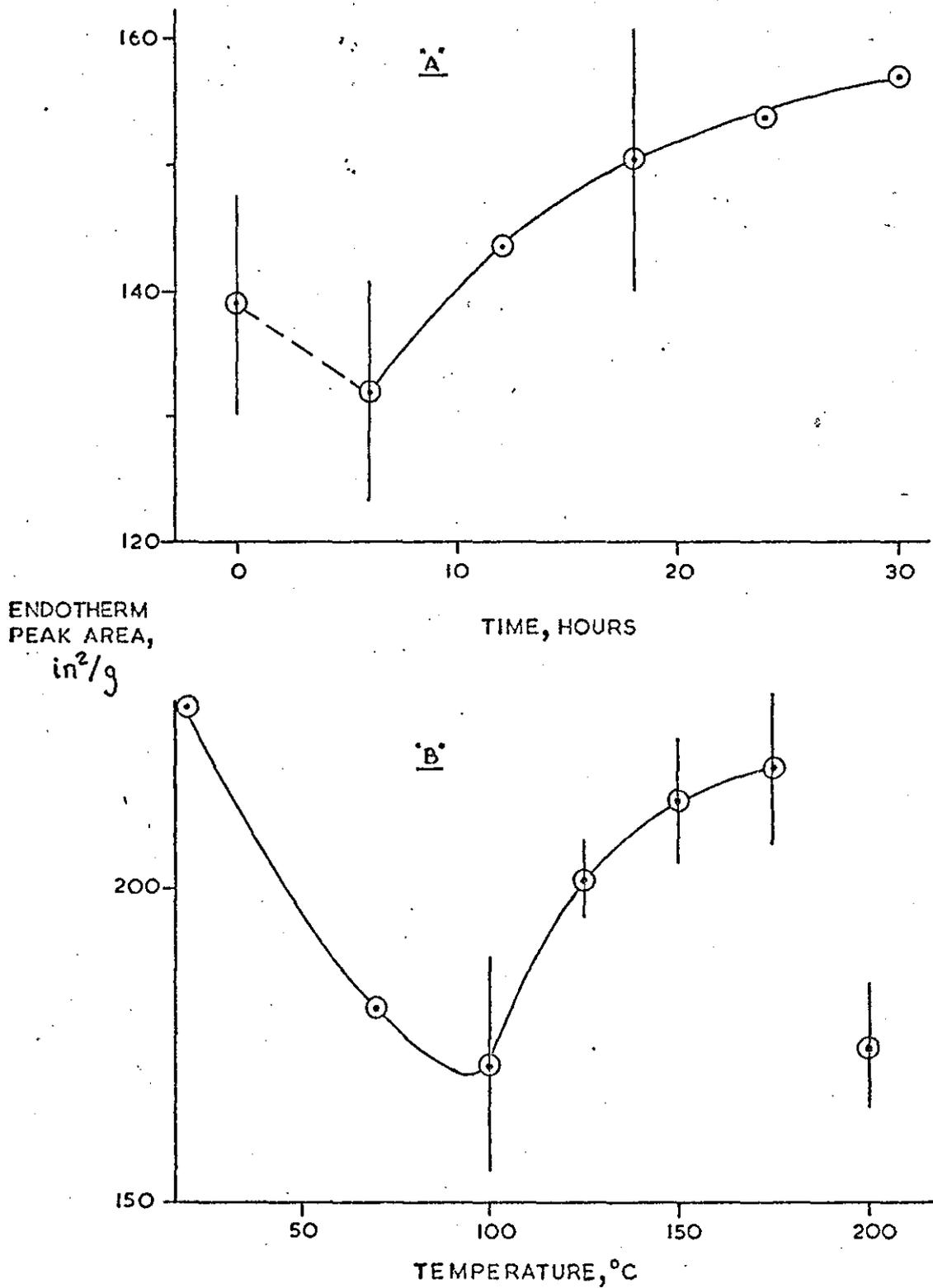


Figure 6.2 Effect of heat treatment on the heat of melting of E303 containing 32 phr of Aerosil 300

"A" Treatment temperature 100°C

"B" Treatment time 24 hours

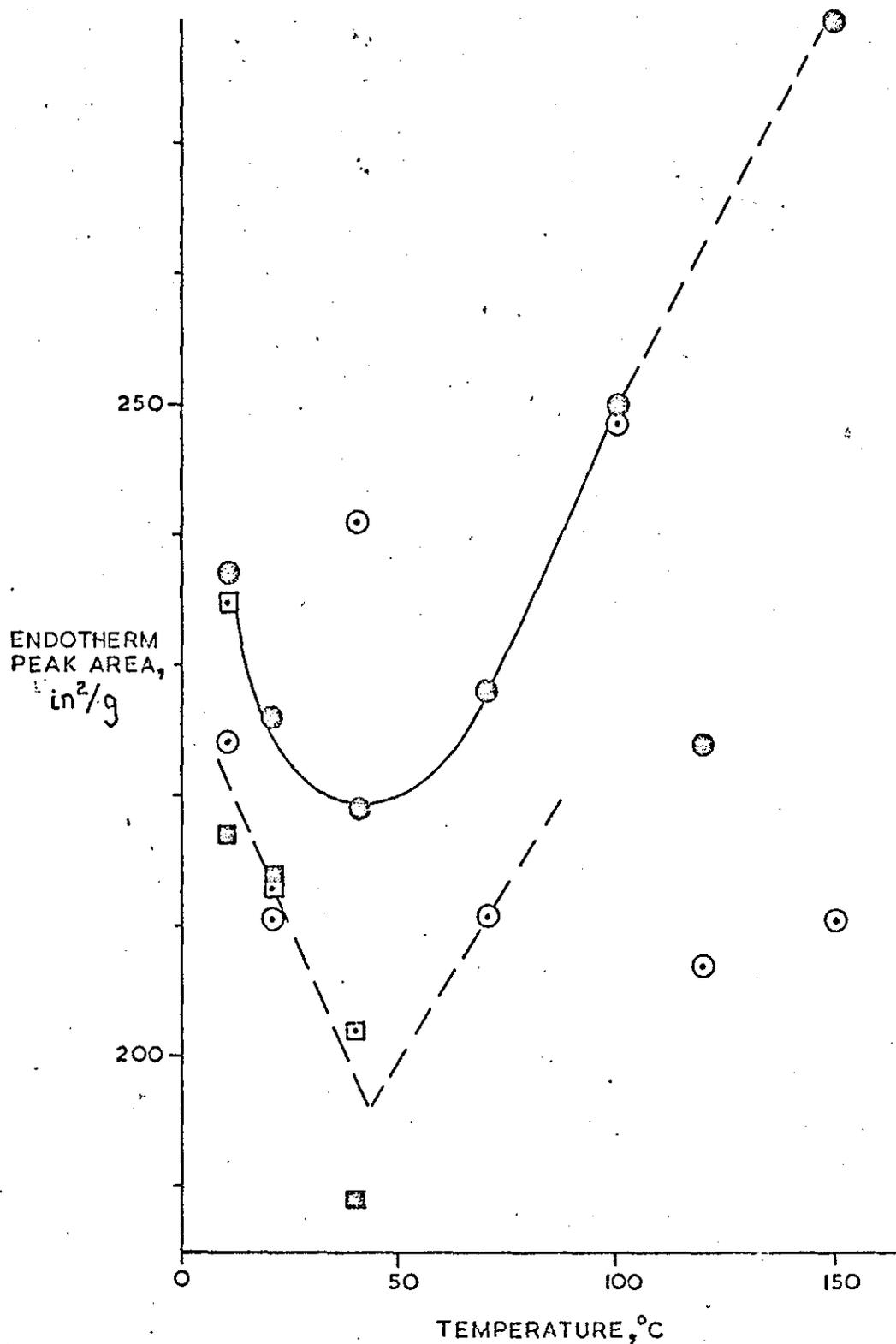


Figure 6.3 Effect of heat treatment temperature on the heat of melting of E303 containing 32 phr of EP 154; and effect of consecutive testing "sessions" (○ 1 ● 2 □ 3 ■ 4)

between sessions although they were run consecutively: however results on material heated at 40°C steadily decreased from session to session: values following treatment at 120°C and above were apparently depressed as for previous 200°C values (Figure 6.2B). The width of the recorded peaks was not constant and this factor may have affected the reproducibility: it can only be concluded that EP 154 was fairly similar to Aerosil 300 in its effect on E303 even though it had a very different effect on apparent hardness (Table 6.1). Similarly, remilling of a bin-aged sample which reduced the apparent hardness from 60 to 28 IRHD had no effect on the heat of melting.

#### 6.4 EFFECT OF RATE OF COOLING

The effect of rate of cooling on the crystallisation was investigated as a possible source of some of the variability. There was found to be a variable effect on the area of the melting endotherm peak and on its broadening which could be so extensive as to give a double peak. It was dependent on such factors as

- a) polymer molecular weight
- b) filler type and concentration
- c) bin-ageing time.

The heats of melting are not reported as they are not directly relevant but they further revealed the difficulties of obtaining reliable data on the crystallisation of silicone rubber, particularly in the presence of filler. They further indicated that low molecular weight polysiloxanes were not suitable model

Table 6.1 Effect of filler surface,  
bin-ageing time and temperature  
of treatment for 24 hours, on  
apparent hardness, IRHD of E303

Filler (32 phr)	Normal (Aerosil 300)		Surface treated (EP 154)	
	1	6	1	6
Time since heat treatment, days				
Heat treatment temperature, °C				
8	42	51	< 28	< 10
room temp.	44	52	< 28	< 10
40	51	54	< 28	< 10
70	55	57	< 28	< 10
100	55	55	< 28	< 10
120	57	58	< 28	13

compounds for the study of rubber-filler interactions, at least where crystallisation was involved.

### 6.5 CONCLUSIONS

Aerosil 300 reduces the heat of melting of silicone rubber by an amount which is dependent on concentration and bin-ageing time (or treatment time or temperature): EP 154 has a similar effect.

It appears that the effect diminishes as the particle size of the filler increases but that it is not markedly affected by filler surface treatment, even though the latter has a very large effect on many other properties e.g. apparent hardness, breakdown time and Young's modulus.

With normal fillers polymer adsorption is presumed to reduce the amount of crystallisation by restricting segmental motion in the vicinity of the filler roughly in line with particle size, thus accounting for the decrease in heat of melting on bin-ageing. With further development of adsorbed rubber and interparticular rubber there may eventually be sufficient concentration of aligned chains near the filler surface to permit those segments to crystallise again, thus accounting for the subsequent increase in the heat of melting.

The greater effect of intermediate filler concentration is probably due to a normal concentration effect up to that intermediate concentration followed by some overloading effect at even higher concentrations e.g.

bound rubber only increases proportionally to the logarithm of filler concentration.

With surface treatment reducing the potential for production of adsorbed rubber and interparticular rubber, although not eliminating it in the case of EP 154, some different explanation is required. Although Aerosil 300 can, after sufficient bin-ageing and remilling etc., behave like EP 154 in some respects, the two fillers behave differently in the short term.

It therefore appears necessary to invoke a purely physical explanation for the heat of melting changes although it is still surprising that the effects are so similar in magnitude and rate. Baker, Charlesby and Morris (1968) similarly proposed physical interaction, but with a range of fillers in silicone rubber at high strains.

Although the heat of melting was not very reproducible an attempt was made to use an Arrhenius plot to estimate the activation energy of the time dependent changes in E303 containing 32 phr of Aerosil 300. Rates were calculated from the time to minimum heat of melting at room temperature (Figure 6.1) and at 100°C (Figure 6.2A); and temperature was calculated for a rate of one reciprocal day (Figure 6.2B). An estimate was made of

the uncertainty of each value and plotted against the reciprocal of the temperature (K). It was found possible to draw a straight line, almost passing through the three ranges (Figure 6.4), from which an activation energy of approximately 0.05 MJ/mol was calculated: this is rather low for chemisorption yet high for a polymer diffusion rate dependent effect.

It remains possible that the heat of melting is a measure of the physical movement of the polymer in the region of the filler but that it is not substantially affected by any reactions in the vicinity of the filler surface; however such reactions would restrict movement of other polymer segments and may account for the temperature for the minimum being less with EP 154 (Figure 6.3) than with Aerosil 300 (Figure 6.2B). Similarly the shorter time to minimum heat of melting when portions were stored under nitrogen may have been due to lesser reaction in the absence of moisture assumed to have been present in the portions stored in air (Figure 10.2).

The formation of adsorbed rubber and interparticular rubber with untreated silica is not precluded, even if the heat of melting is only affected by the physical effects of filler particles on the mobility of polymer chains in their vicinity.

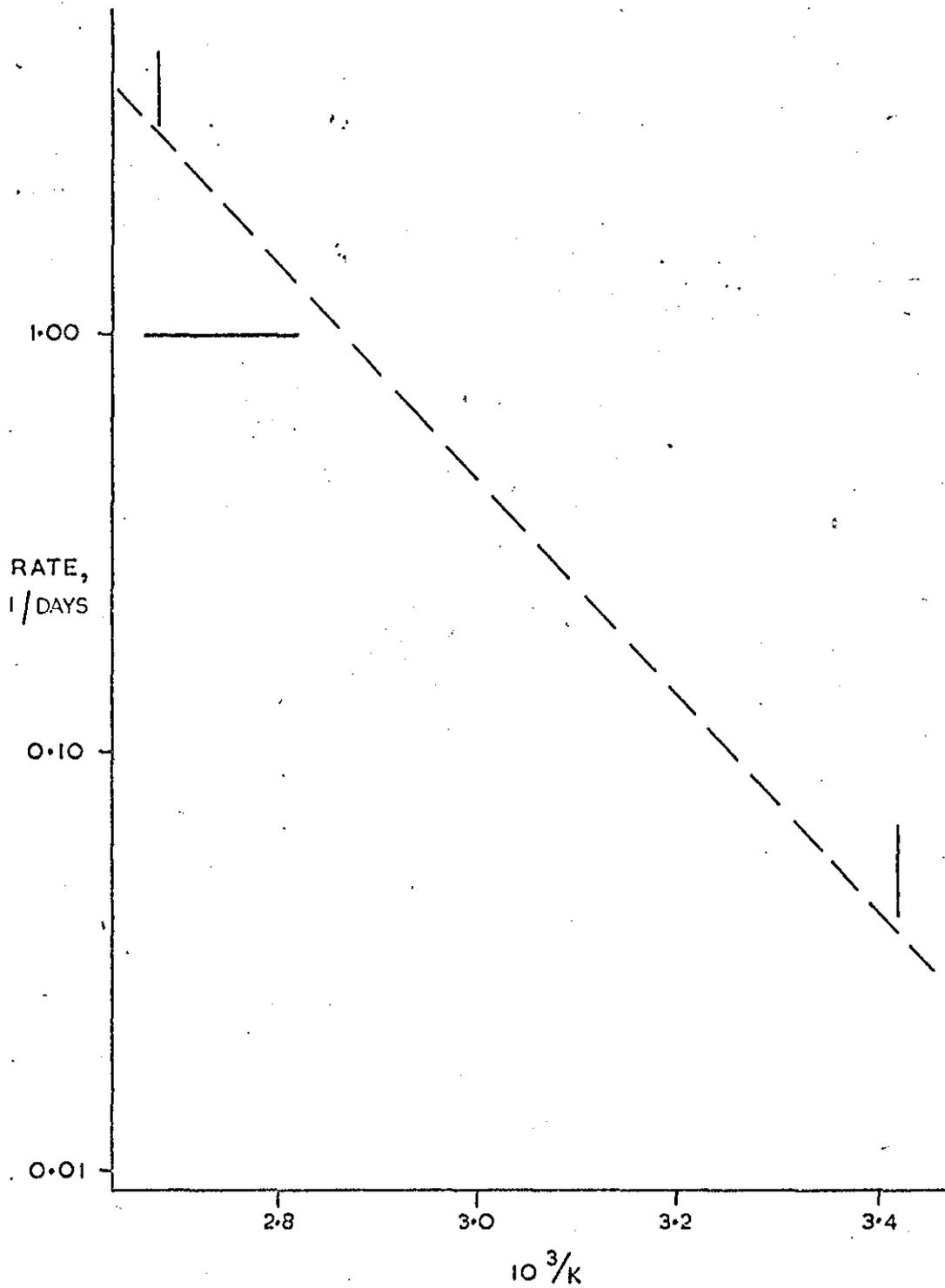


Figure 6.4 Arrhenius plot of estimated reciprocal days to minimum heat of melting and bin-ageing/treatment temperature (K) for E303 containing 32 phr of Aerosil 300

## CHAPTER 7 MISCELLANEOUS PHYSICAL PROPERTIES

### 7.1 REBOUND RESILIENCE

Resilience of E302 containing Aerosil 300 increased on bin-ageing and with increase in filler concentration (Figure 7.1): slightly lower values were obtained when samples were bin-aged in a polyethylene bag to restrict effects of moisture in the atmosphere rather than on the laboratory bench. A dependence on moisture content was confirmed in E302 using Aerosil 300 with adjusted water content (Figure 7.2).

The increase in resilience is comparable to the increase in many other physical properties and provides further evidence for the development of a three-dimensional structure on bin-ageing of silicone rubber containing Aerosil 300. The higher values, indicating further interaction, in the presence of moisture are consistent with increases in breakdown time in mixes bin-aged in a humid atmosphere (Southwart 1969 2).

### 7.2 VISCOSITY

Curometer amplitude (Figure 7.3) of E302 containing Aerosil 300 (10 to 20 phr) decreased on bin-ageing and with increase of filler concentration indicating an increase in viscosity; this increase was less when

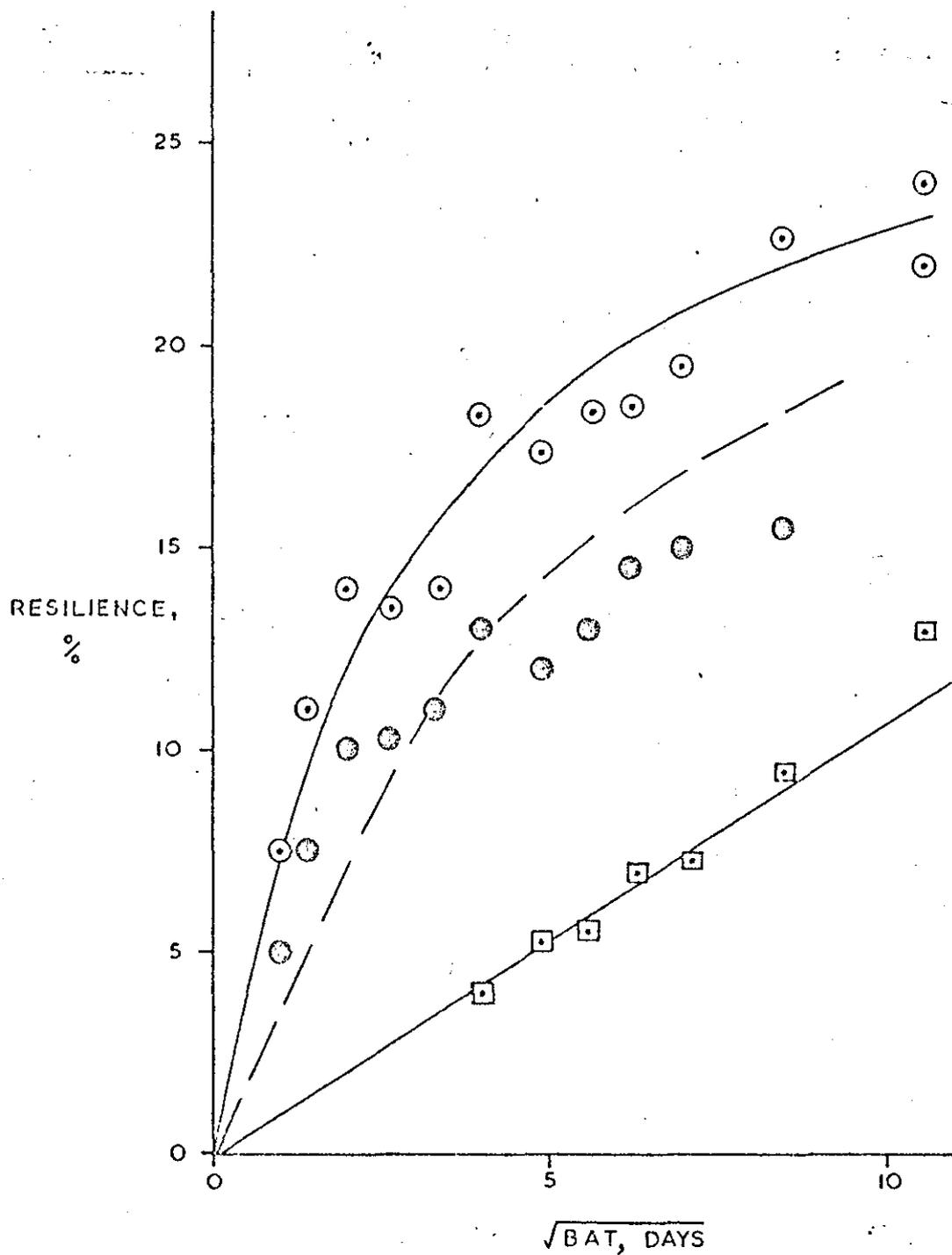


Figure 7.1 Dependence of rebound resilience of E302 on the square root of bin-ageing time and concentration of Aerosil 300 ( $\square$  20 phr  $\odot$  30 phr  $\circ$  40 phr)

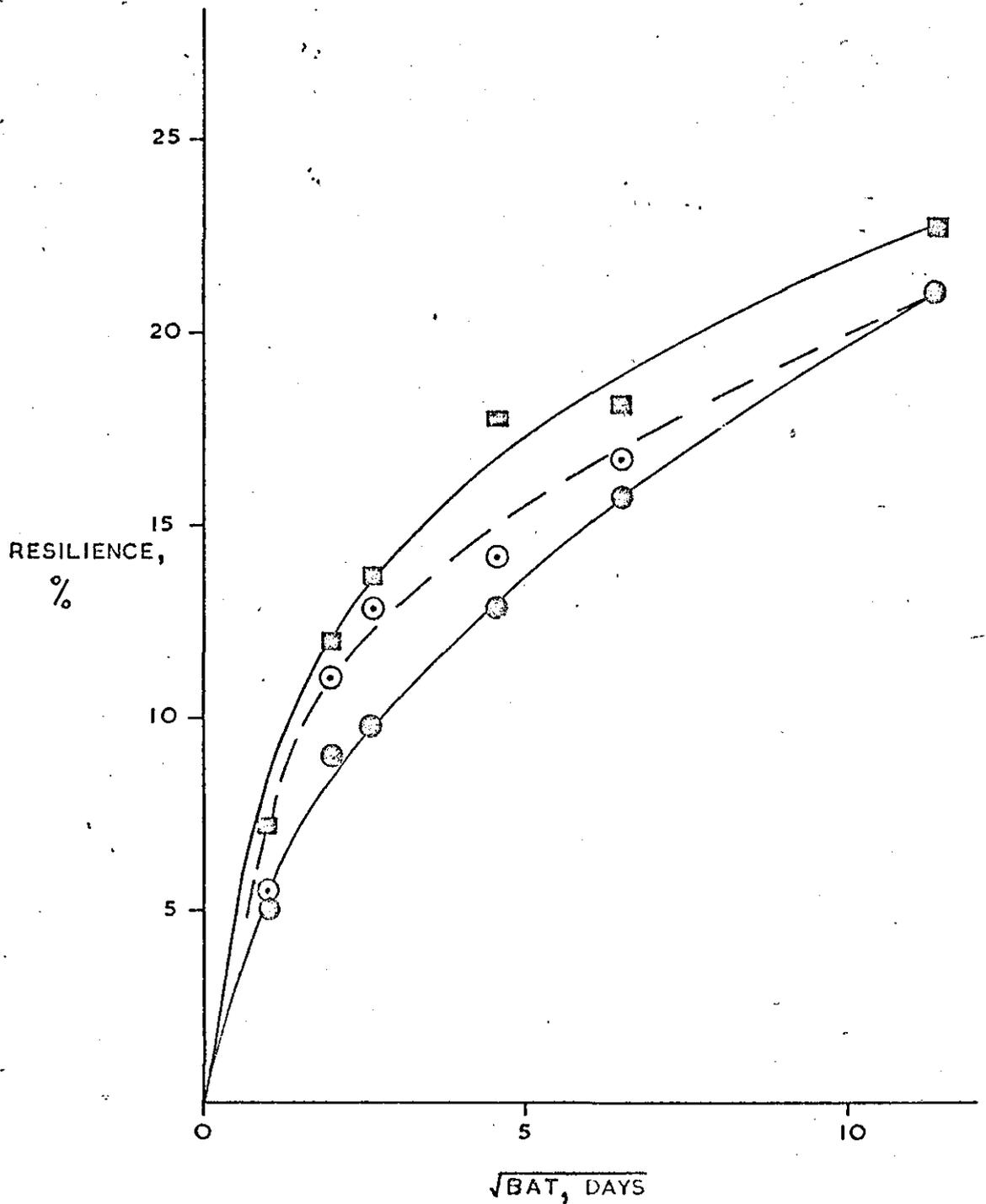


Figure 7.2 Dependence of rebound resilience of E302 on the square root of bin-ageing time, and concentration of filler and moisture

Legend	Aerosil 300, phr	Water, phr
○	28.5	3.5
⊙	32.0	-
■	32.0	4.0

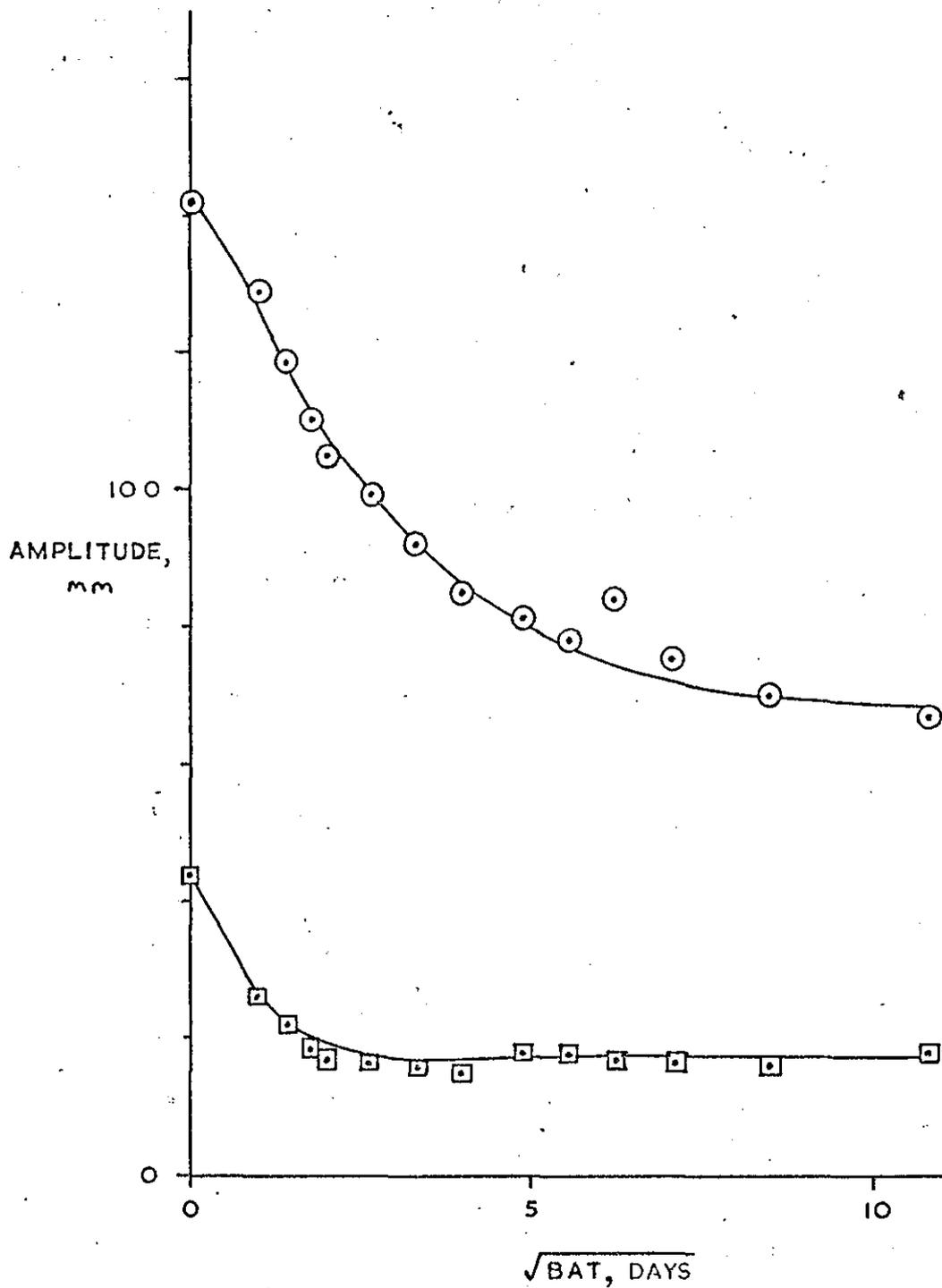


Figure 7.3 Dependence of Curometer amplitude of E302 on the square root of bin-aging time, and concentration of Aerosil 300 (  $\odot$  10 phr  $\square$  20 phr )

bin-ageing was conducted in a polyethylene bag.

E302 containing higher concentrations of Aerosil 300 (30 to 40 phr) was too stiff for satisfactory values to be obtained on the same instrumental setting but later values were obtained, with higher applied stress, for E302 with wet and dry Aerosil 300 as in Section 7.1. The values (Figure 7.4) showed the same relative effect of moisture etc. as for resilience, with 36 phr of wet Aerosil 300 just exhibiting the highest viscosity (lowest amplitude). Prolonged bin-ageing gave, in all cases, the reversal of the stiffening only just shown, by breakdown time, in Figures 3.1 and 3.2.

As the reversal of viscosity increase appears to have occurred after less bin-ageing than the processibility change, and to have been greater in magnitude, it implies that the processibility is due to a secondary effect of some structural change. The relatively mild shearing probably enables the Curometer to give a reasonable indication of the existing three-dimensional structures whereas the processibility value (breakdown time) reflects differences in the behaviour of that structure when subjected to severe shearing on the mill.

The values of Curometer amplitude of E303 increased in the expected order with four different fillers (Table 7.1) but relative magnitudes were different from those in other

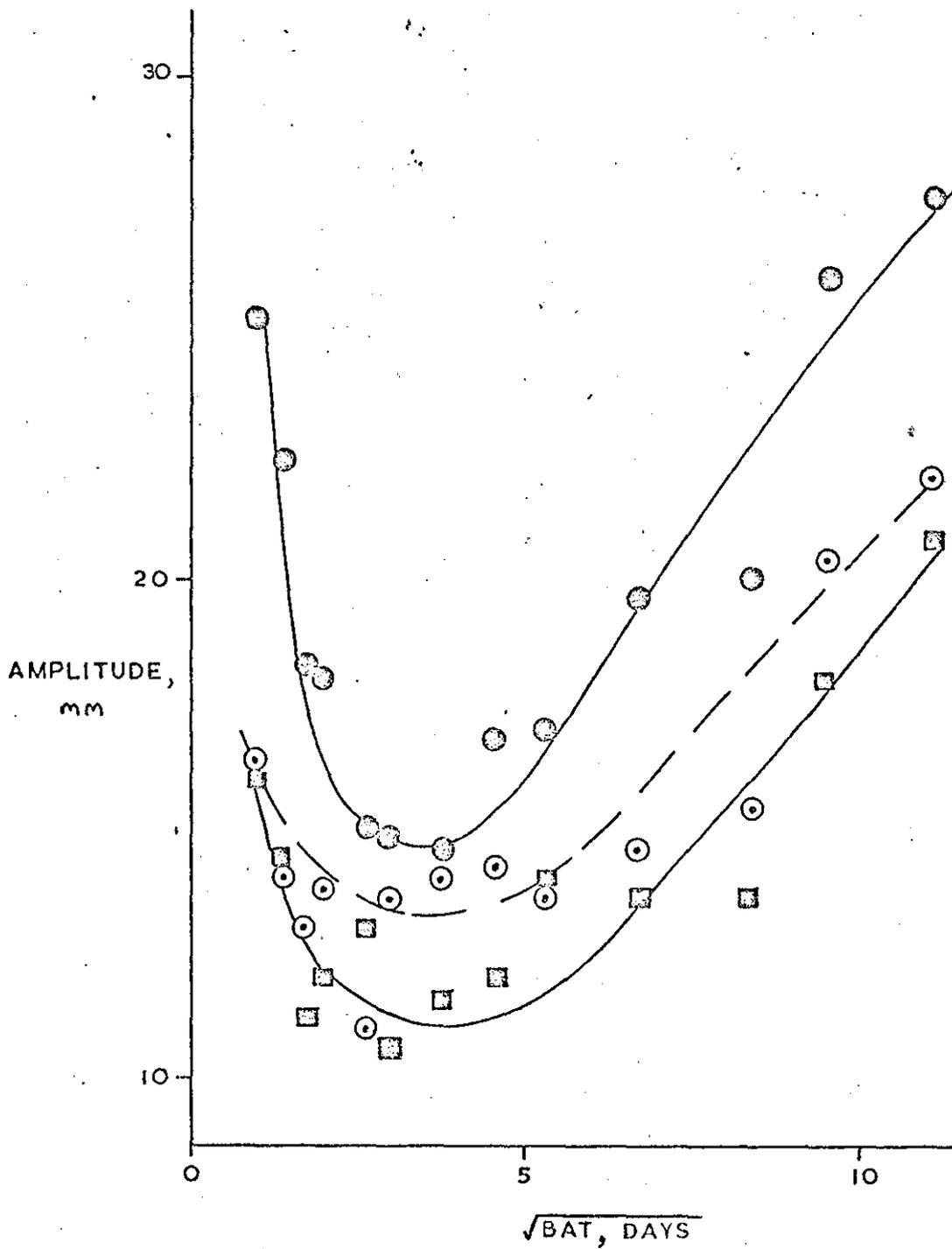


Figure 7.4 Dependence of Curometer amplitude of E302 on the square root of bin-aging time, and concentration of filler and moisture (legend as for Figure 7.2)

Table 7.1 Effect of fillers on the Curometer amplitude of E303

Mix history \ Filler*	Aerosil 300	Aerosil 200	EP 154	Celite Superfloss
Immediately after mixing	1.0	1.5	1.7	8.5
Bin-aged 1 week	NP	NP	1.3	8.0
Bin-aged 8 weeks	NP	NP	1.0	6.8
1 day at 70°C	1.2	1.7	2.0	9.5
8 weeks at 70°C	NP	NP	1.2	7.0
Remilled after 1 day at 70°C	2.5	2.0	2.0	9.5

\* 32 phr

NP mix too stiff for Curometer determination

properties e.g. Young's modulus (Table 5.5); again this was probably due to a dependence on actual strain conditions.

There are two points of similarity with heat of melting. Firstly, EP 154 behaved more like Aerosil 300 than Celite Superfloss; secondly there was a distinct minimum on bin-ageing.

### 7.3 WEIGHT LOSS

The weight loss of the lower molecular weight batch of E302, which gave a higher rate of increase of breakdown time (Figure 3.3) and higher rate of increase of Young's modulus on bin-ageing (Section 5.1.1), was higher than that of a batch of normal molecular weight, particularly at 200°C and higher temperatures (Table 7.2).

In the presence of 30 phr of Aerosil 300 weight losses were almost independent of polymer molecular weight. In both cases the filler exhibited some stabilising effect, but dramatically so with the lower molecular weight polymer (Table 7.2).

Table 7.2 Effect of molecular weight and  
Aerosil 300 on the weight  
loss (%) of E302 on heating

Molecular weight		0.46 x 10 <sup>6</sup>		0.83 x 10 <sup>6</sup>	
Temperature	Time	Unfilled	Filled*	Unfilled	Filled*
150°C	1 hour	7.6	6.7	7.2	7.0
	1 day	12.8	9.7	13.5	10.4
	1 week	13.8	10.0	13.9	10.7
200°C	1 hour	11.5	8.4	11.4	9.1
	1 day	19.7	10.0	13.9	10.8
	1 week	31.2	10.7	14.6	11.1
250°C	1 hour	19.2	9.0	13.6	10.0
	1 day	90.2	10.0	20.1	13.2
	1 week	95.4	19.0	29.7	21.3
305°C	1 hour	97.8	10.4	20.9	11.4
	1 day	99.8	22.3	34.5	20.9
	1 week	100.0	29.5	36.2	27.0

\* 30 phr of Aerosil 300

PREFACE TO CHAPTER 8

SUMMARY OF PRINCIPAL RESULTS

1. Breakdown time increases on bin-ageing but eventually exhibits a maximum; it generally decreases when test-pieces are successively remilled.
2. Bound rubber increases monotonically on bin-ageing but rarely, if ever, is equilibrium achieved. After prolonged bin-ageing, remilling does not significantly reduce bound rubber.
3. Liquid absorption is dependent on the mean distance between filler particles.
4. Young's modulus and hardness increase to equilibrium values on bin-ageing but are decreased by remilling.
5. Heat of melting passes through a minimum on bin-ageing.
6. Activation energy apparently decreases on bin-ageing.
7. Resilience increases on bin-ageing.
8. Curometer viscosity decreases on bin-ageing but sometimes exhibits a minimum.
9. Effects increase with increase in the specific surface area, and in the concentration, of the filler. They are much less with a hydrophobic filler, except in the case of heat of melting.

## CHAPTER 8 DISCUSSION

### 8.1 INTRODUCTION

There is clearly some interaction during, and following, mixing of silicone rubber and a filler such as Aerosil 300 on a rubber mill. The effects are so different from those of simple peroxide crosslinking of silicone rubber that polymer-polymer interaction is concluded to play little or no part. This still however leaves the two possibilities of polymer-filler interaction and filler-filler interaction; both of which are theoretically possible although there is some doubt whether the former will be physical or chemical in nature (see Appendix 2).

As mentioned in Chapter 1 and further amplified in Appendix 2, the author's proposed structures are not unique, moreover they are not yet fully defined, so it is useful to restate the terms and equate them with other workers' ideas, thus revealing areas of uncertainty.

Many workers have considered that some rubber is closely associated with individual filler particles or aggregates, with the result that there have been many references to "shell of rubber" etc; often this has been considered as bound rubber. More recently reference has been made to rubber "occluded" within filler aggregates, rather than bound outside, and evidence has been presented that some fraction of the dibutyl phthalate absorption of carbon

black better accounts for reinforcement than does bound rubber. Whether this rubber is bound outside the aggregates or occluded within the aggregates, or more likely some of each, it is included in the author's adsorbed rubber.

Similarly there have been references to "multicontact adsorption (on different particles)", "polymer chains joining filler particles", "bound rubber bridgehead chains" etc: all these are included in the author's interparticular rubber.

As often implied by others, these two structures were first considered to be independent structures but it is now proposed that a given polymer chain can exist in both forms with these acting substantially independently. For example, the essential product of interparticular rubber is a three-dimensional structure, yet the segments in contact with filler will be able to behave substantially like adsorbed rubber, even before scission of the interparticular rubber converts them into adsorbed rubber only: this is the picture also envisaged by Gessler (1969).

In these general terms it is now possible to consider in detail the effect of typical mixing, bin-ageing and remilling cycles of the silicone rubber-silica system.

## 8.2 EFFECT OF SILICA IN UNVULCANISED SILICONE RUBBER

In the free state a filler such as Aerosil 300 exists as aggregates of ultimate particles; on addition to silicone rubber on the mill these aggregates begin to disperse and increase the viscosity of the mix, whether or not there is specific interaction between polymer and filler. This increase in viscosity assists in the breakdown of filler aggregates thus increasing any polymer-filler interaction.

On completion of mixing, interaction is found to have occurred as the mix is elastic and some of the rubber cannot be extracted by a good solvent; on bin-ageing these effects are magnified. There must be some three-dimensional structure to confer this elasticity but it could be filler-filler structure or interparticular rubber or both.

On returning the mix to the mill this structure is broken down but the time taken (BDT) appears to be too great for it to be due simply to breaking of filler-filler structures weakly held by van der Waals forces. It is, however, consistent with two competing reactions, such as the breakage and reformation of polymer-filler "bonds" where a slow change from interparticular rubber to a more favoured adsorbed rubber would give the observed effect. Due to the higher viscosity of this mix when first returned to the mill there will be further breakdown of filler aggregates and thus increased chance of polymer-filler interaction: in the extreme the interaction is believed to increase the rate of interparticular rubber

formation so much that the mix can crepe-harden: this only occurs when bin-ageing time is low, presumably while the concentration of adsorbed rubber is still low.

Whereas physical properties reflecting the interparticular rubber e.g. Young's modulus, are reduced by this remilling, the bound rubber, being the sum of adsorbed rubber and interparticular rubber is not consistently affected: dependent on the bin-ageing time bound rubber can be slightly increased or decreased by the remilling (Southwart 1969 2). On bin-ageing, most physical properties increase again, sometimes to even higher values than previously, due to the improved filler dispersion. However, the relatively low rate of increase is not consistent with the normally rapid reformation of filler-filler structures.

On subsequent remillings, Young's modulus, breakdown time etc decrease again, with reduced thixotropy, whereas bound rubber is even less affected than on the first remilling. Where bin-ageing is effectively accelerated by heat treatment, remilling has a similar effect and again there is sometimes little thixotropy. These changes are not consistent with breakdown and reformation of filler-filler structures but they are consistent with the breakdown of interparticular rubber and increase of adsorbed rubber: except when interparticular rubber is broken twice between two given filler particles, and molecular weight of extracts appears

to rule this out, it remains as adsorbed rubber, in matrix rubber, with properties comparable to those of EP 154 in silicone rubber, except again for high bound rubber. Even if filler-filler structures were largely responsible for the initial elasticity of the system they clearly do not survive the repeated bin-ageing and remilling; only gross scission of the polymer could reduce the Young's modulus etc. so drastically and, in the absence of an occluding structure, the polymer should be readily extractable. That it remains virtually unextractable is very strong evidence for adsorbed rubber which can in turn protect the filler from interaction with itself, as proposed by Pocknell et al with silicone oil (1969). Such protection implies that at least some of the rubber is on the outside of aggregates, rather than completely occluded.

Consideration of liquid absorption has been excluded so far. It seems unlikely that filler-filler structures could account for the swelling results recorded even if they have elastic properties but they have now been excluded for other reasons. Some other structure is required to account for the liquid absorption which can be virtually independent of bin-ageing and immersion times, and it has already been proposed in Section 4.8 that this arises from interparticular rubber forming a three-dimensional structure with filler particles. The reduction in liquid absorption of mixes bin-aged after remilling can again be attributed to improved filler dispersion and thus reduced particle separation.

Normally the filler effects were in line with their accepted reinforcing powers i.e. interaction increased as particle size decreased, or perhaps more relevant, as surface area increased. The principal exception was EP 154 where surface treatment reduced much of the polymer-filler interaction to be expected of such a small particle size filler yet hardly affected the heat of melting.

### 8.3 NATURE OF THE INTERACTION BETWEEN SILICA AND SILICONE RUBBER

The tendency for many of the properties of the silicone rubber-silica system to change at a rate proportional to the square root of time implies that the reactions involved are controlled by the self-diffusion of the polymer to the filler surface: this is partly supported by the activation energy of approximately 0.038 MJ/mol calculated from the time to maximum breakdown time (Section 3.2), compared with the self diffusion rate of silicone rubber of 0.016 MJ/mol (van Amerongen 1964).

In Section 4.1.3 the initial rate of development of bound rubber however gave an activation energy of approximately 0.08 MJ/mol consistent with chemical reaction. With the higher concentration of matrix rubber during, and immediately after, mixing it is less likely that polymer diffusion will be a controlling factor, so that the true nature of the reaction is observed. A change from true chemical adsorption to a diffusion dependent interaction could also account for the change

in the rate of development of bound rubber (Figure 4.5) etc. Similarly the larger bound rubber values following successive immersion and drying, compared with continuous immersion, could be due to an increased rate of diffusion in the presence of liquid: as this also decreases the swelling (Table 4.14) the extra adsorption must be interparticular and can therefore only occur during the drying stage when filler particles are sufficiently close together. Reduction of polymer molecular weight which should increase the diffusion rate did effectively reduce the time to maximum breakdown time (Figure 3.3).

Berry and Cayré (1960) concluded that diffusion of polymeric free radicals controlled the development of bound rubber in milled mixes even in the first 24 hours, accounting for an activation energy of only 0.04 MJ/mol (Appendix 2) in spite of the chemical reaction involved. Although the ineffectiveness of DPPH indicates that the current interactions are not due to free radicals, polymer diffusion is still important: the difference may be due to the greater initial mobility of silicone rubber molecules compared with styrene-butadiene polymeric radicals. Other workers have obtained values of approximately 0.08 MJ/mol (Section 1.3) following both solution mixing and mill mixing: these were attributed to chemisorption.

Further evidence for chemisorption is provided by the action of morpholine, a powerful catalyst for siloxane condensation etc, in increasing the structure formation during mixing (Section 3.6) and the rate of development of bound rubber (Section 4.1.3). Continued exposure led to a considerable decrease in bound rubber such as had only previously been found with water (Southwart 1969 2).

It is not possible from these results to differentiate between the various types of siloxane-bond reactions but they are all generally reversible; however, interparticular rubber, due to its greater number of siloxane bonds, and its isolation from filler particles, is more likely to suffer scission by hydrolysis than is adsorbed rubber; once the filler is protected by adsorbed rubber such broken chains will not be able to be re-adsorbed. This is comparable to the changes postulated to account for decreases in breakdown time except that multiple scission of a given interparticular rubber segment to produce soluble rubber is more likely to result from hydrolysis than from mechanical working.

Such chemisorption of polymer on filler will be dependent on the availability of reactive groups on the filler surface and thus will increase with increase of filler surface area and concentration, but be low with treated filler e.g. EP 154. Although an empirical relationship was established in Figure 4.2 between bound rubber and

the logarithm of the filler concentration (phr) a simple concentration effect would require the bound rubber to be directly proportional to the filler concentration. Vondráček and Schätz (1973) however reported a decrease in specific bound rubber content (polymer weight (g) per  $100 \text{ m}^2$  of filler surface area) above a contact area of approximately  $15 \text{ m}^2/\text{g}$  (polymer) i.e. 19 phr of a lower surface area Aerosil ( $80 \text{ m}^2/\text{g}$ ). Converting their values to the same units as Figure 4.2 gave a good approximation (Figure 8.1) to similar linearity up to 30 phr of filler: their values were high because they were obtained after bin-ageing until equilibrium "hardening" had been obtained in the equivalent of 10,000 hours or more at room temperature. Their "hardening", which was revealed by penetrometer measurements, was directly related to bound rubber but only for samples not remilled. They obtained activation energies of "hardening" and bound rubber formation of only approximately  $0.04 \text{ MJ/mol}$  and attributed them to hydrogen bonding between polymer and filler, irrespective of surface treatment: except immediately after mixing the current values of activation energy are in good agreement with that value.

It is therefore proposed that steric hindrances etc. do not become operative at some limiting concentration below which bound rubber is proportional to filler concentration but operate over all practical concentrations, with additional filler always having an exponentially

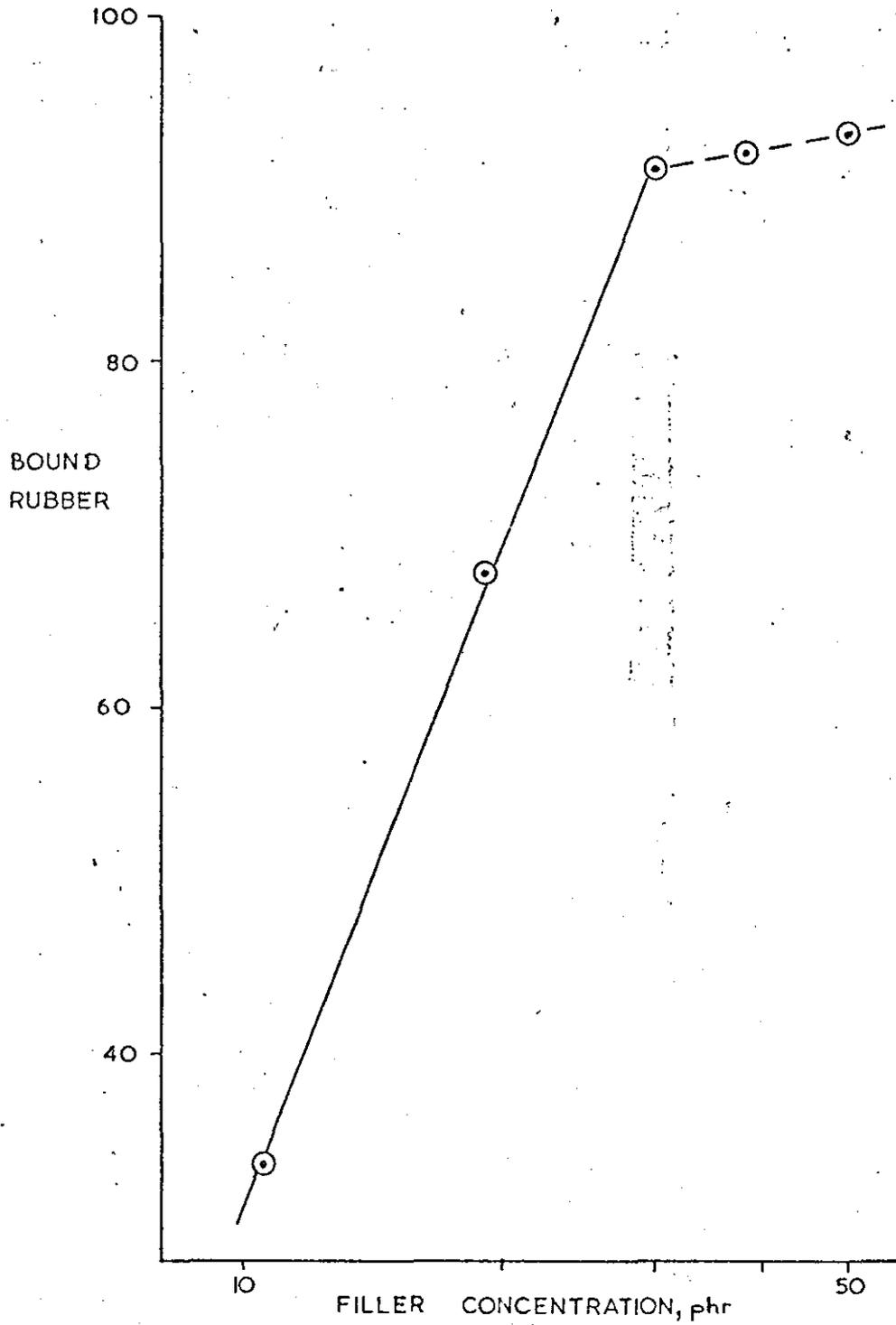


Figure 8.1 Relationship between bound rubber and filler concentration for silicone rubber containing Aerosil 130 (data from Vondráček 1974)

decreasing effect. This is probably due to reduced mobility of polymer chains once part has been adsorbed on filler particles or occluded in filler aggregates, as suggested for heat of melting effects (Section 6.5).

The current work thus supports the view that the interaction between polymer and filler is chemical in nature but often with apparently lower activation energy due to the rate dependence of polymer diffusion to the filler. Nevertheless, the activation energy is higher than that of self-diffusion of the polymer due to restrictions imposed by polymer adsorption etc.

Although similar values could be due to hydrogen bonding, as suggested by Vondráček and Schätz (1973) it seems unlikely that the resultant structures would survive swelling in hexane; furthermore, moisture would tend to hydrogen bond preferentially to the filler thus reducing polymer-filler interaction, contrary to the observed effects.

#### 8.4 PROPERTIES OF THE UNVULCANISED SILICONE RUBBER - SILICA SYSTEM

Many of these have been considered in Section 8.2 in establishing the validity of the proposal of adsorbed rubber, interparticular rubber and matrix rubber but they will now be re-examined in an attempt to quantify the structures and further define the adsorbed rubber for which several possibilities exist, varying from short polymer chains adsorbed at one point but with the

greater part of their length in the matrix rubber, to multi-site adsorption with the greater part of their length adsorbed on the filler surface (or occluded).

Although modulus has often been used to quantify interparticular rubber by application of elasticity relationships this is not acceptable where some of the interacted rubber (as adsorbed rubber) may only affect the modulus by hydrodynamic effect (Appendix 2): it may not even be acceptable in the presence of filler and absence of adsorbed rubber.

The differences between the modulus values, particularly between Young's modulus and hardness (Section 5.6), indicate a more open structure than in a vulcanised system, as could result from interparticular rubber: however these differences cannot yet be analysed quantitatively. Similarly a property such as breakdown time can only indicate a change in interparticular rubber but not its absolute value.

Heat of melting, by revealing the tendency of the system to crystallise, is sensitive to structural changes occurring on bin-ageing etc. but these are mainly due to the slow re-orientation of the polymer following addition of a fine particle filler rather than to differences, at the filler surface, between Aerosil 300 and EP 154.

In many ways the most interesting aspects of the findings are bound rubber and swelling; the latter being widely used to determine crosslink density of vulcanisates using the Flory-Rehner equation (Appendix 2). This is well established for gum vulcanisates where the necessary conditions of uniform distribution of crosslinks and equilibrium can be met; again the validity in filled vulcanisates is questioned and many variations have been proposed to attempt to overcome possible deficiencies. The most promising of these has recently been proposed by Brennan (1971): by assuming that the curatives in a rubber-filler mix were confined to matrix rubber he found that swelling values fell on one line when plotted against a function of his curative concentration irrespective of black type and concentration. This appears to require the rubber to be very closely associated with the filler, as proposed by Gessler (1969): Medalia (1973 1) has rejected the idea but not given any justification for his rejection.

There are clearly problems in interpreting the swelling behaviour of the silicone rubber-silica system; although the structure proposed earlier, dependent mainly on the spatial distribution of filler particles (Section 4.7), remains attractive, it does not easily differentiate between different forms of adsorbed rubber. If the rubber is occluded or so tightly adsorbed on the filler that it cannot be affected by solvent it can be regarded as filler: if much of it exists freely between filler particles it cannot, as Blow (1973)

pointed out, - swell but its presence will reduce the activity of the liquid in the gel although less so than matrix rubber. Such differences would be difficult to detect and would probably be overshadowed by other changes such as polymer slippage on the filler surface or rearrangement etc. to increase effectively the length of interparticular rubber under the prolonged swelling action of a liquid.

One of the big differences between the current silicone rubber-silica system and earlier published work, has been the enormous time sometimes required to extract all the soluble rubber and it has been suggested that this could be due to solubilisation of rubber during the immersion. The earlier work was with organic rubber-carbon black systems and, on the occasions when extraction was definitely taken to equilibrium, relatively short immersion periods were required. It is now proposed that soluble silicone rubber is genuinely difficult to extract. Partly because of its high molecular weight which makes it sensitive to the size of the network "windows" through which it is extracted and partly because of the enormous reduction in the size of the "windows" if these are defined by the separation of such fine filler particles as Aerosil 300. Rate of extraction of soluble rubber from a gum vulcanisate increased with decrease in peroxide concentration (Figure 4.4) while in unvulcanised rubber it increased

with decrease of filler concentration (Figure 4.1): similarly the amount extracted from a gum vulcanisate increased with increase in network expansion and soluble rubber extracted by a good solvent was of higher molecular weight than that previously extracted by a poor solvent (Section 4.2.1).

It is necessary to examine Blow's (1973) recent analysis of the author's earlier results in the light of the proposed theory. It is accepted that the partition coefficient was independent of solution concentration for any given sample although there was some doubt whether equilibrium conditions had been established. However, the present work with the gum vulcanisates confirmed that apparent partition coefficient was indeed constant (Figure 4.7): values were obtained from the difference in rubber content between samples immersed in pure liquid and in solution, and are classed as apparent because further soluble rubber was present in most samples, as shown by the values at zero solution concentration. This prevents the determination of equilibrium bound rubber after limited immersion time. The constant factor was the crosslink density of the gel and it is proposed that this controls the partition coefficient: it has been established (Boyer 1945; Southwart 1969 2) that the change in swelling per unit of polymer in solution increases as gel crosslink density decreases, this being equivalent to an increase in partition coefficient.

In the presence of filler there will be a similar effect due to the filler-interparticular rubber network but, as shown by the values in Figure 4.9, the partition coefficient was not constant. For the samples previously extracted to equilibrium bound rubber the sample not bin-aged had probably not sufficiently interacted before immersion; however the partition coefficients after 1 and 4 days bin-ageing were almost equal and certainly not proportional to the equilibrium bound rubber: their near equality however is consistent with a dependence on the proposed network.

Although it is possible to draw lines through the low concentration values for unextracted samples in Figure 4.9, parallel to the lines for the extracted samples, the better lines, as drawn in Figure 4.9 converge near the fully bound rubber line and fall on the continuous line in Figure 4.10 when related to their bound rubber as determined (this was virtually an equilibrium value in one case). Unfortunately no samples were immersed long enough to establish equilibrium in solution.

Insufficient results have been obtained to quantify the adsorbed rubber, interparticular rubber, matrix rubber and partition coefficient. On the other hand none of the results is inconsistent with the proposal of filler particles with their adsorbed rubber, "joined" by interparticular rubber into a three-dimensional structure,

controlling the absorption of liquid and desorption of matrix rubber. Such a structure will be dependent on the average distance (D) between filler particles, related to the diameter (d) of the particles and their volume concentration (c) by the expression:-

$$D = (\pi/6c)^{\frac{1}{3}} d \quad \dots (3)$$

The data of Figure 4.26 are replotted in Figure 8.2 and show a direct relationship between the particle separation calculated from equation (3) and the weight of toluene absorbed ( $S_p$ ).

#### 8.5 PROPERTIES OF THE VULCANISED RUBBER-FILLER SYSTEM

The effect of the introduction of peroxide crosslinks into the system will be dependent upon the structures present at the time and these will probably alter during the vulcanisation due to the accelerating effect of the high temperature. The structure of the vulcanisate will therefore be very complex and it is not surprising that it is difficult to define (Blanchard 1973).

However it is only in the vulcanisate that it is possible to relate physical properties in the presence of filler to those in its absence and the classical example of this is the Guth-Gold relationship (Appendix 2).

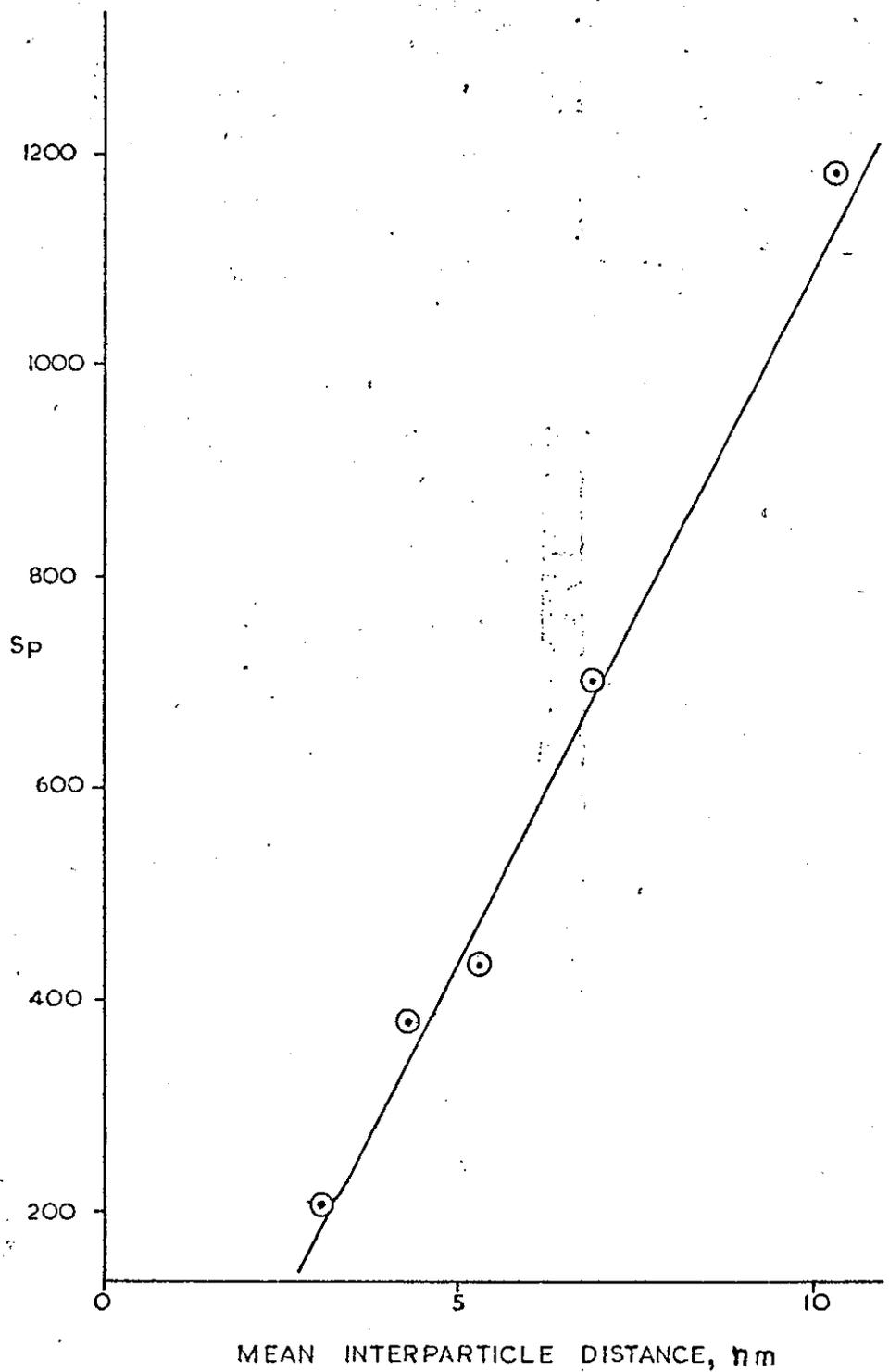


Figure 8.2 Relationship between liquid absorption (Sp) of E302, from Figure 4.26, and mean distance between Aerosil 300 particles

It was shown in Chapter 5 that neither Aerosil 300 nor SAF black agreed with the Young's modulus version of the simple Guth-Gold equation:-

$$E = E_0 (1 + 2.5c + 14.1c^2) \dots (2)$$

Furthermore Minusil, MT black and Ballotini differed in their Young's modulus - filler concentration relationship.

To apply the concept of reinforcement volume it is necessary to estimate the bound rubber and this has been shown to be extremely difficult with Aerosil 300 in silicone rubber. Using previously published estimated values, and the assumption that bound rubber formation during vulcanisation was equivalent to that of one day at room temperature (Southwart and Hunt 1969), to calculate reinforcement volume  $\phi$  for the initial Young's modulus values, and using 2 day bound rubber values (an empirical choice) for the final Young's modulus values, the two curves were found to be consistent (Figure 8.3) and in much better agreement with the modified Guth-Gold equation (Appendix 2):-

$$E = E_0 (1 + 2.5\phi + 14.1\phi^2) \dots (4)$$

Similar treatment of a number of fillers using the bound rubber values determined after subjecting mixes to the same heating cycle as for vulcanisation gave,

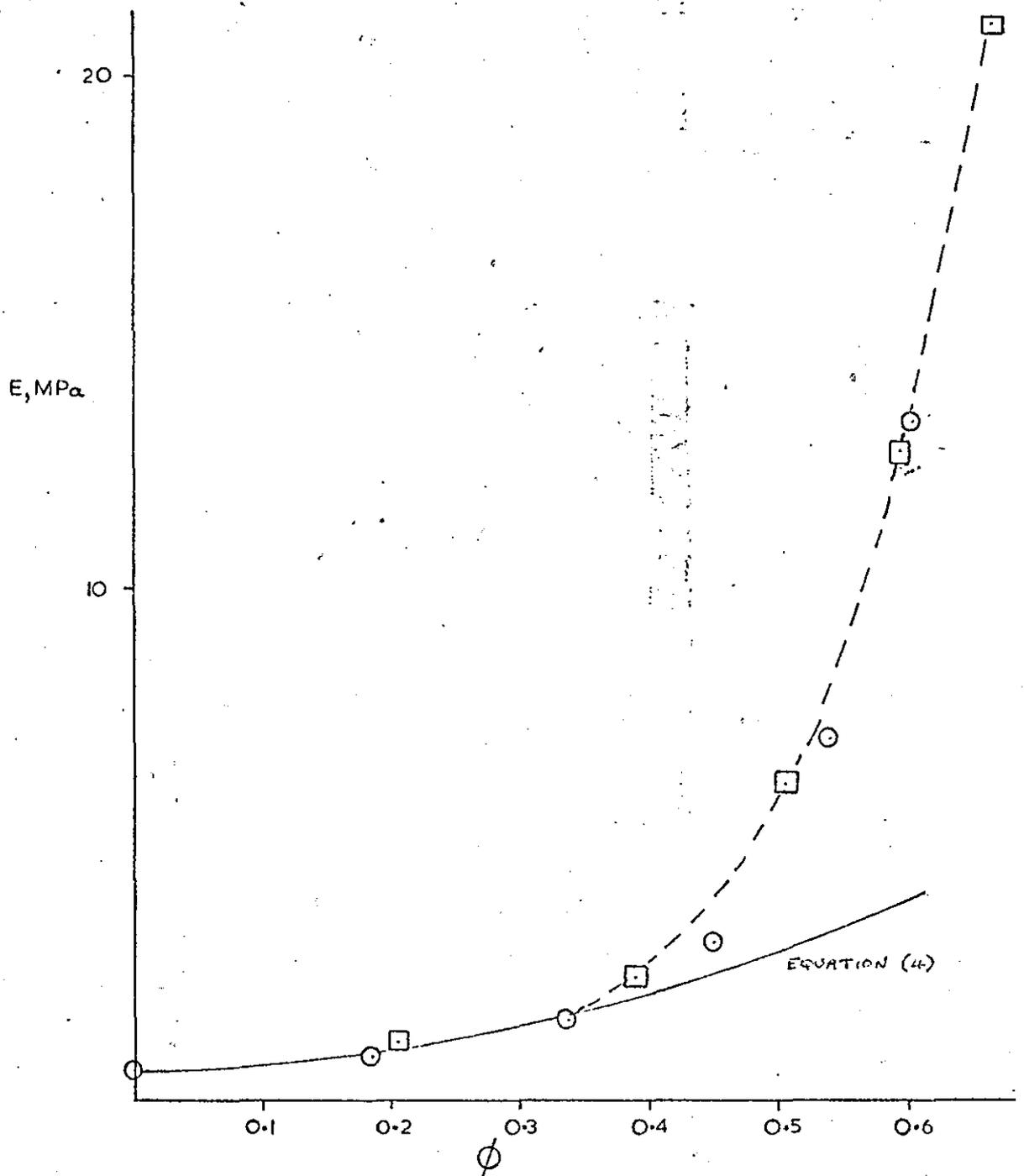


Figure 8.3 Relationship between Young's modulus ( $E$ ) of vulcanised E302 and reinforcement volume ( $\phi$ ), immediately after mixing (○) and at equilibrium (◻)

in Figure 8.4 many points between the Oberth and van der Poel lines (Appendix 2) and revealed the principal exceptions of SAF black and Celite Superfloss, both asymmetric fillers but with the latter's asymmetry arising not from aggregates of spherical particles but from a genuine asymmetry of the crushed fossils.

Whereas the normal modification applied for asymmetric fillers is:-

$$E = E_0 (1 + 0.67fc + 1.62f^2c^2) \dots (5)$$

it is considered more relevant to combine equations (4) and (5) to allow for both bound rubber and asymmetry:-

$$E = E_0 (1 + 0.67f_1\phi + 1.62f_1^2\phi^2) \dots (6)$$

where  $f_1$  is the asymmetry factor for an asymmetric filler with its bound rubber.

Even assuming a simple linear relationship between filler concentration and bound rubber for SAF black the small amount of bound rubber involved (16 per 75 phr) decreases the value of  $f = 6$  required for equation (5) to  $f_1 = 4$  required for equation (6), as shown in Figure 8.5.

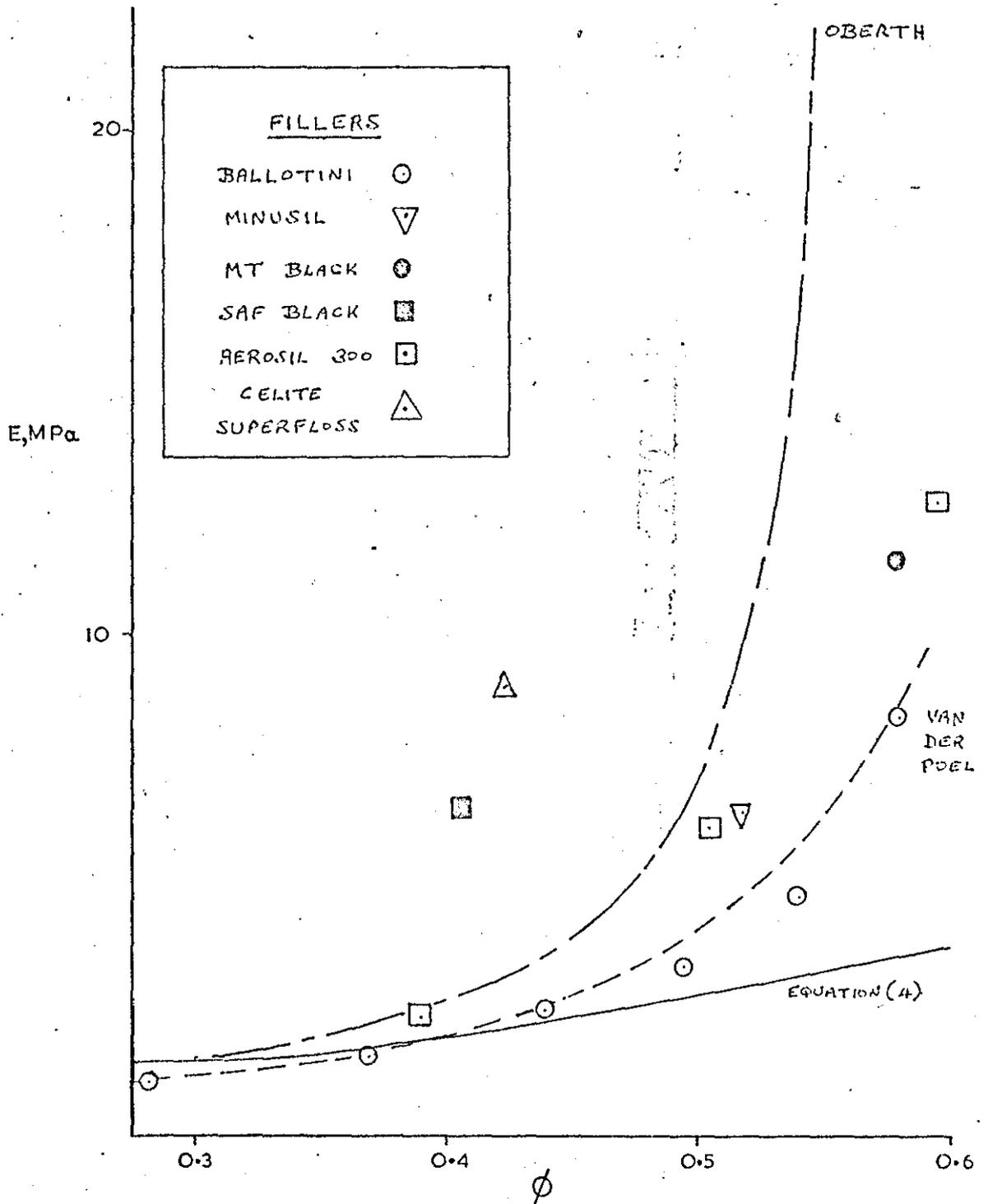


Figure 8.4 Relationship between Young's modulus ( $E$ ) and reinforcement volume ( $\phi$ ) of a number of fillers in vulcanised E302 in comparison with "predicted" values

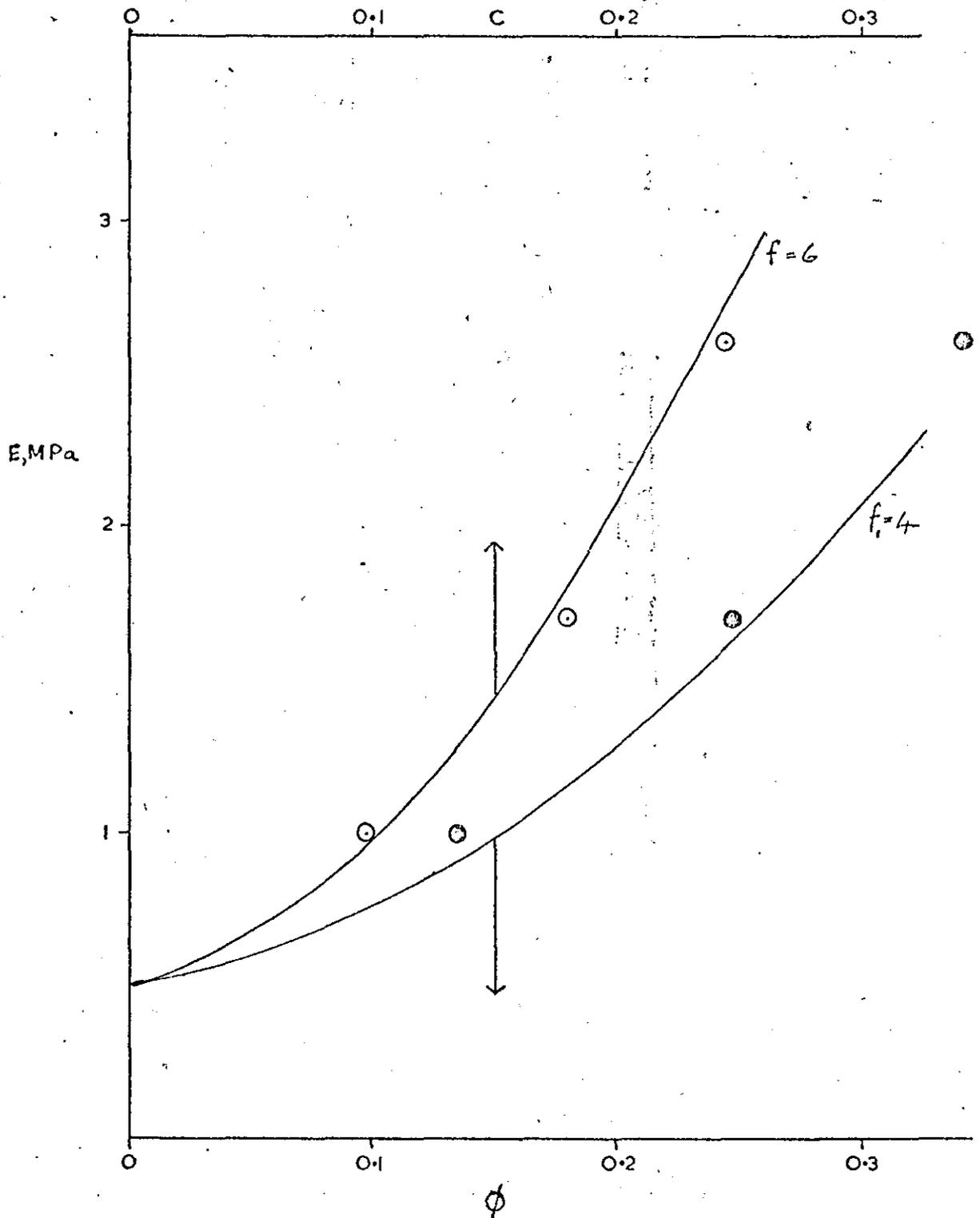


Figure 8.5 Relationship between Young's modulus ( $E$ ) of vulcanised E302, volume concentration of SAF black ( $c$ ), reinforcement volume ( $\phi$ ), shape factors ( $f$  and  $f_1$ ), equation (5)  $\odot$  and equation (6)  $\bullet$

In spite of the uncertainties about precise values of bound rubber the Young's modulus - bound rubber relationship for the silicone rubber-silica system certainly provides strong evidence for equation (4); similar evidence was reported for Aerosil 300 in natural rubber (Southwart 1969 1).

However, other evidence must be considered. Modulus with HAF black has been found to fit equation (5) under very different circumstances: firstly, for Young's modulus of vulcanised natural rubber, at virtually zero strain (Mullins and Tobin 1965); secondly, for dynamic shear modulus at high strain (1.0) of vulcanised butyl rubber even though values at lower strains were very much higher (Appendix 2). This implies that the high dynamic values at low strain, attributed to filler-filler structure, are essentially due to the dynamic stresses and that they would be ineffective at very low strains as indicated by Voet and Aboytes (1970). Payne (1965) only reported a small increase in modulus with increase of frequency but the values in Figure 10.9 show a bigger effect of frequency, particularly at the lower strains; however, the later results established that the dynamic modulus on the first cycle was virtually equal to the Young's modulus. Re-examination of the previous workers' values however reveals that the low strain moduli are very similar and that the apparent difference

in behaviour is due largely to the difference in gum vulcanisate values. Even in silicone rubber Young's modulus has a similar value in the presence of SAF black (Figure 5.5) thus indicating that the effect is largely independent of the rubber, as shown by Payne (1965) when he determined the shear modulus of HAF black in paraffin.

Stress enhancement by filler diminishes as strain is increased in a single extension (Figure 5.10) and the Young's modulus of a material stress-softened by several extensions to a given stress or strain, is reduced and only recovers slowly and partially (Figure 5.15). Although bound rubber has not been determined on stress-softened material the limited decrease during the much more severe action of remilling an unvulcanised sample indicates that reduced modulus etc. cannot be attributed to reduced bound rubber and its effect on equations (4) or (6). Similarly the promoter treatment of silica leading to almost complete elimination of filler-filler effects on dynamic modulus (Payne 1965) is assumed to have increased the bound rubber, probably by production of adsorbed rubber which protects the filler from itself.

It is concluded that the present results have shown that Guth-Gold type equations are of only limited value in explaining reinforcement effects, partly due to the

complex effect of filler-filler and other structures. The results do not invalidate the proposed structures but rather indicate that a clearer understanding is required so that adsorbed rubber can be included in the calculation of the reinforcement volume while interparticular rubber and the effective crosslinks it introduces can be used to modify  $E_0$  values, as proposed by Bueche and others. Although filler-filler structures cannot explain all the observed effects they clearly play an important role in some of them.

## CHAPTER 9 CONCLUSIONS

### 9.1 PROCESSIBILITY

Apart from the stiffening due to normal hydrodynamic effects of filler on rubber viscosity, the viscosity of a silicone rubber-silica mix is increased due to stronger interaction between rubber and filler. Such stronger interaction also occurs in some organic rubber-filler mixes and in all such cases it contributes to a decrease in processibility but perhaps to a greater extent in silicone rubber - fine particle fume silica mixes.

There are however important differences in the latter which explain the differences described in Section 1.2: similar effects may indeed occur with organic rubber but to such lesser extent that they have escaped detection. These differences are attributed to the specific interaction between the chemically similar materials - silicone rubber and silica - and their rate of reaction, whether in condensation, siloxane rearrangement or hydrolysis. Much of this reaction is believed to be chemical in nature although diffusion of reactive species can be the rate determining step.

These differences are consistent with the proposed molecular structure of adsorbed rubber, interparticular rubber and matrix rubber but with the strong possibility

also of three-dimensional filler-filler structures.

The various structures form during bin-ageing but processibility is dependent mainly on the changes occurring during mechanical working, particularly remilling, thus making the breakdown time a very important parameter. The changes are largely controlled by the amount of adsorbed rubber present as this in turn controls the amount of interparticular rubber which can be formed, following creation of further reactive species either by improved dispersion of the filler or scission of existing bonds.

Commercially it is necessary to keep breakdown time as low as possible but ideally to have a stable system once that breakdown processing is completed. The present work has shown that breakdown time can decrease on bin-ageing but mixes remain thixotropic: although the total processing time to confer stability is generally less than for a mix reprocessed fairly soon after mixing the net result is not commercially advantageous, with the possible exception of crepe-hardened mixes which would normally have been discarded. The situation is more promising where the changes are accelerated by heat treatment because both the breakdown time and the thixotropy can be usefully reduced, given the correct conditions.

It is the establishment of correct conditions which is so difficult with these systems and indeed the lack of reproducibility was largely responsible for the initiation of a research programme of which the present work is a part.

Such lack of reproducibility is not now surprising in view of the nature of the reactions proposed: some of these sources of variation have been revealed by the acceleration of the decrease in processibility as the molecular weight of the polymer is decreased, by the presence of additional moisture and most markedly by the presence of a condensation catalyst. Even these effects are due to different causes: molecular weight affects the breaking up of the filler aggregates and the diffusion rate of the polymer, whereas moisture and a condensation catalyst affect the rate of condensation, rearrangement and hydrolysis of siloxane bonds. The latter possibly also help to explain the apparently lower extent of reaction with E351 where phenyl groups increase the hydrolysis rate (Polmanteer 1970).

## 9.2 PHYSICAL PROPERTIES OF THE SILICONE RUBBER-SILICA SYSTEM

Although it has not been possible to prove the existence of adsorbed rubber and interparticular rubber, the physical properties determined are consistent with these proposed structures. The changes in physical

properties on bin-ageing, heat treatment and remilling are consistent with the changes in processibility.

Stress exhibited the increase commonly attributed to increases in network structure but comparison of individual properties e.g. Young's modulus and hardness, gives support to the proposed structure rather than to the simpler structures often proposed elsewhere e.g. a shell of rubber on the filler or occluded rubber or interparticular rubber: in effect the proposed structure incorporates all these other proposals, with changes in the concentration of the "components" held responsible for many of the recorded changes in properties.

The use of gum vulcanisates with residual sol rubber has established that the latter is difficult to extract, even using good solvents, and that the amount extracted is dependent on the expansion of the network. This has provided strong circumstantial evidence that the low rate of extraction from unvulcanised silicone rubber-silica mixes previously discussed is due to a low rate of diffusion of the rubber rather than to the desorption of rubber from the filler surface.

The discovery that, in some cases, the amount of solvent absorbed remained substantially constant while sol rubber was being extracted, has led to the

proposal that interparticular rubber produces a three-dimensional network based on the filler particles as they are distributed within the polymer by the mixing process and by any subsequent reprocessing. Thus solvent absorption is largely controlled by the interparticle distances and their effect on the length of the interparticular rubber segments rather than by the amount of adsorbed rubber: it is thus largely independent of the amount of bound rubber whether this is interpreted as:-

- (a) true bound rubber i.e. adsorbed rubber plus interparticular rubber
- (b) equilibrium bound rubber as determined i.e.
  - (a) plus any matrix rubber which, although theoretically soluble cannot be extracted by the solvent from its constrained condition
- (c) non-equilibrium bound rubber i.e. (b) plus any extractable rubber not yet extracted.

This is not to deny any dependence on bound rubber, and indeed there is still some evidence for a direct relationship between bound rubber and swelling, but the dependence arises because there is some relationship between the filler particle size and reactivity on the one hand, and the amount of adsorbed rubber, interparticular rubber and interparticle distance on the other.

The ability of the silicone rubber to crystallise at low temperature was also affected by fine particle fume silica but the interrelationship of effects was clearly different. It is proposed that the addition of fine particles disturbs the molecular orientation of polysiloxane chains for a time in the vicinity of filler particles but that eventually they reorient there irrespective of the precise configuration on the filler surface.

### 9.3 REINFORCEMENT THEORY

The proposed structures for the polymer are also presumed to exist in organic rubbers but their effects may be quite different. Firstly their rate of formation, and destruction, is likely to be completely different due to the different character of both polymer and carbon black. Secondly the interparticle distances with carbon black will be generally greater.

Assuming similar structures it can be seen to be imprudent to attempt to explain reinforcement by Guth-Gold type equations incorporating either adsorbed rubber allowances or interparticular rubber allowances: rather is it necessary to include allowances for both. In many cases there will also be some strain-dependent effect of filler-filler structure:

In an organic rubber-carbon black mix the interparticular rubber may be a much smaller percentage of the bound rubber so that the latter fairly reasonably indicates the adsorbed rubber content. Therefore Brennan (1971)

probably obtained his results because he had adequately estimated the amount of matrix rubber and interparticular rubber and the curative concentration used to vulcanise them. He may have got much less convincing results had he used Aerosil 300 instead of carbon black but he might then have been able to calculate the amount of interparticular rubber from the correction necessary to his curative concentration and then, by subtraction from the bound rubber, to obtain his adsorbed rubber.

#### 9.4 FURTHER WORK

On commercial grounds further investigation of processibility and physical properties of silicone rubber is required after acceleration of the interaction with filler by heat treatment, preferably during mixing as already used by some silicone rubber manufacturers, or by chemical acceleration.

Similar work is required for the more expensive fluorosilicone rubbers and it is hoped to be able to use a Wallace-RAPRA micro-mill for this purpose to obtain breakdown times on much smaller quantities (approx. 5g).

On more academic grounds further investigation is required of the behaviour of unvulcanised mixes in liquids, including the possible utilisation of Blow's partition coefficient proposal.

Some of the present work could usefully be further extended to organic rubbers particularly by inclusion of fillers such as Aerosil 300 where effects could perhaps be more easily detected. As Blow (1973) suggested, some effects may have been missed in even the natural rubber-carbon black system because of an emphasis on tyre compounds but with supply difficulties developing for carbon blacks the time is particularly opportune to extend organic rubber reinforcement research to include other fillers.

## APPENDIX 1 COLLABORATIVE WORK

### 10.1 DUNLOP RESEARCH CENTRE - CANADA

#### 10.1.1 Stress at low strains

Using a special extensometer in conjunction with an Instron tensile tester the stress of a fluorocarbon rubber vulcanisate was determined, in compression and extension, over the temperature range 100-140°C: similar values were obtained on a natural rubber vulcanisate containing 50 phr of carbon black (HAF) but only at 25°C: strains were varied within the range +0.0253 to -0.0325.

The fluorocarbon results were analysed by computer for agreement with Gaussian and Mooney-Rivlin equations. For the former correlation coefficients were better than 0.9998 but there was a very small zero error. For the latter, correlation coefficients were in the range 0.195 to 0.988 but this was attributed to the indeterminate nature of the Mooney-Rivlin equation at very low strains. However the points on the Mooney-Rivlin plots did not have the zero slope required by the Gaussian equation so it was concluded that the results were in better agreement with the Mooney-Rivlin equation.

This conclusion is not considered generally acceptable because the single set of values with natural rubber approximated to a zero slope of Mooney-Rivlin plot and reference was also made to different behaviour with polybutadiene.

The results for natural rubber are replotted according to Hooke's law in Figure 10.1 and can clearly be interpreted as linear. Even the results for fluorocarbon rubber at 120°C, which gave the highest correlation coefficient for agreement with the Mooney-Rivlin equation, can be interpreted as similarly linear, at least if taken from the origin: slight curvature, however, is apparent when all the results are included.

If the slight zero error, revealed by the computer in the Gaussian plot, had been included in the Mooney-Rivlin plot a different conclusion would probably have been reached.

The results serve to illustrate the difficulties of interpretation of stress-strain curves at low strains, of the order of 0.01, and help to justify the use of the Hookean expression in the current determination of Young's modulus (Section 5.1).

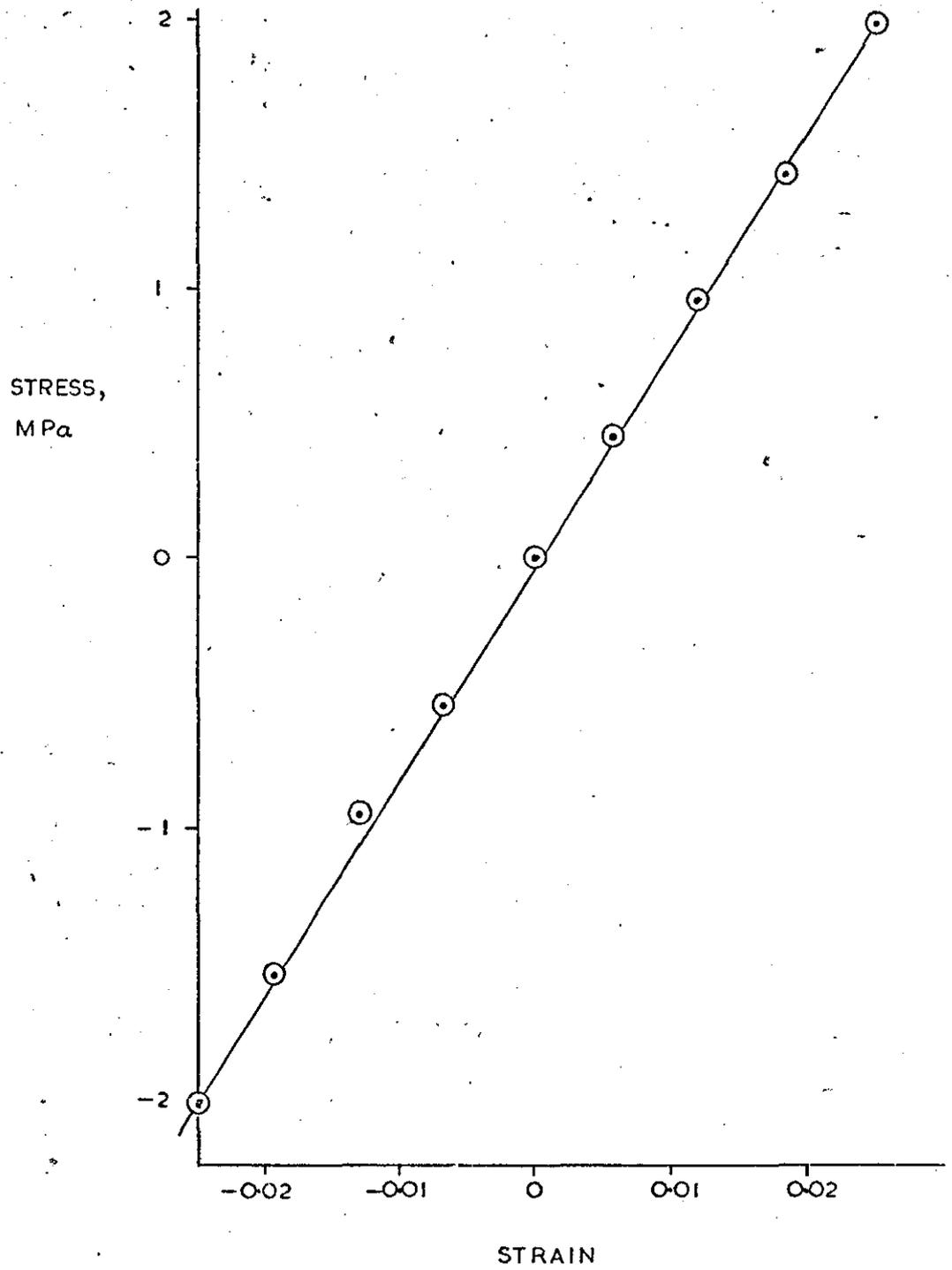


Figure 10.1 Stress-strain relationship for a natural rubber vulcanisate containing 50 phr of HAF black

### 10.1.2 Heat of melting

The heat of melting of E303 containing 32 phr of Aerosil 300 was determined using a Du Pont 950 Thermal Analyser fitted with scale expansion recorders; with the additional use of a planimeter areas were reproducible within  $\pm 2\%$ . Test-pieces were sealed into their containers under nitrogen.

Values were obtained on successive determinations on one test-piece and compared (Figure 10.2) with those obtained using test-pieces freshly sealed from material bin-aged in the laboratory. The values were means of at least two determinations and confirmed the minimum in the heat of melting; they also showed that the minimum was reached more rapidly when successive determinations were made on the same test-piece although this could have been due to bin-ageing effectively in nitrogen rather than (damp) air.

An absolute value of heat of melting of E303 of  $27.9 \pm 0.71$  J/g was obtained following calibration of the instrument using mercury.

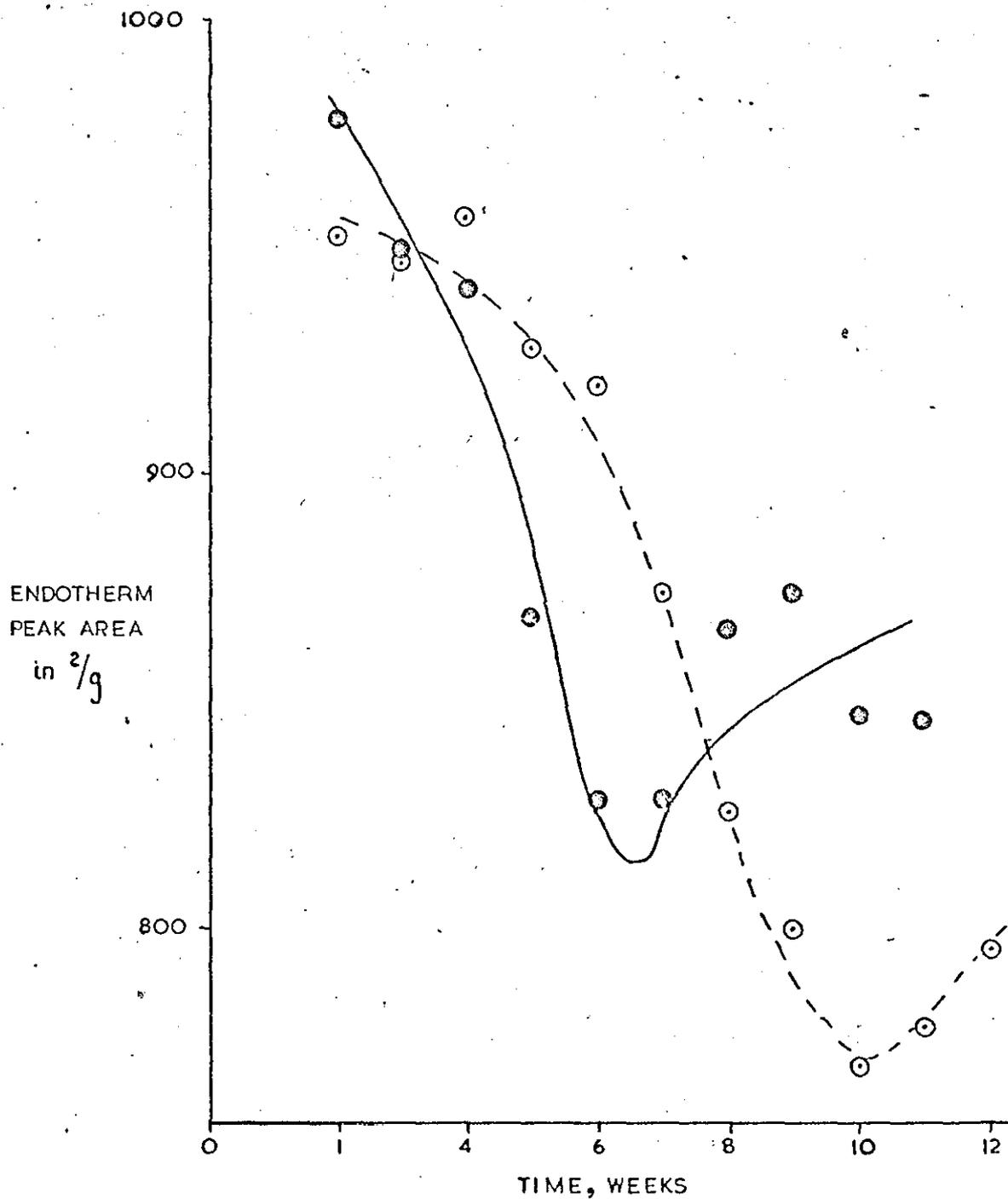


Figure 10.2 Effect of environment and storage time on the heat of melting of E303 containing 32 phr of Aerosil 300

- one hermetically sealed test-piece
- fresh test-piece each week

## 10.2 DUNLOP RESEARCH CENTRE - BIRMINGHAM

### 10.2.1 Failure properties

Log (energy input) was found to be linearly related to log (energy loss) for a series of fillers in SBR and silicone rubber (E351), when vulcanised test-pieces were extended to slightly less than their breaking strain. Slight differences between the two polymers were indicated (Figure 10.3).

Actual tensile strength was found to be almost directly proportional to energy input (Figure 10.4): ultimate tensile strength was similarly related.

The values indicate that tensile strength, energy input and energy loss are all manifestations of the same basic phenomenon, as previously reported for a wide range of carbon blacks in organic rubbers (Bulgin 1971). The energy input was not directly related to the surface area for all fillers, although the values indicated some correlation within certain filler types e.g. carbon blacks in SBR (Figure 10.5).

A different grouping of fillers was found for the relationship between tear strength, determined at 20°C and 5 m/sec, and energy input to tensile failure; silicas (except EP 154 in E351) exhibited higher tear strength than carbon blacks for given energy input (Figure 10.6).

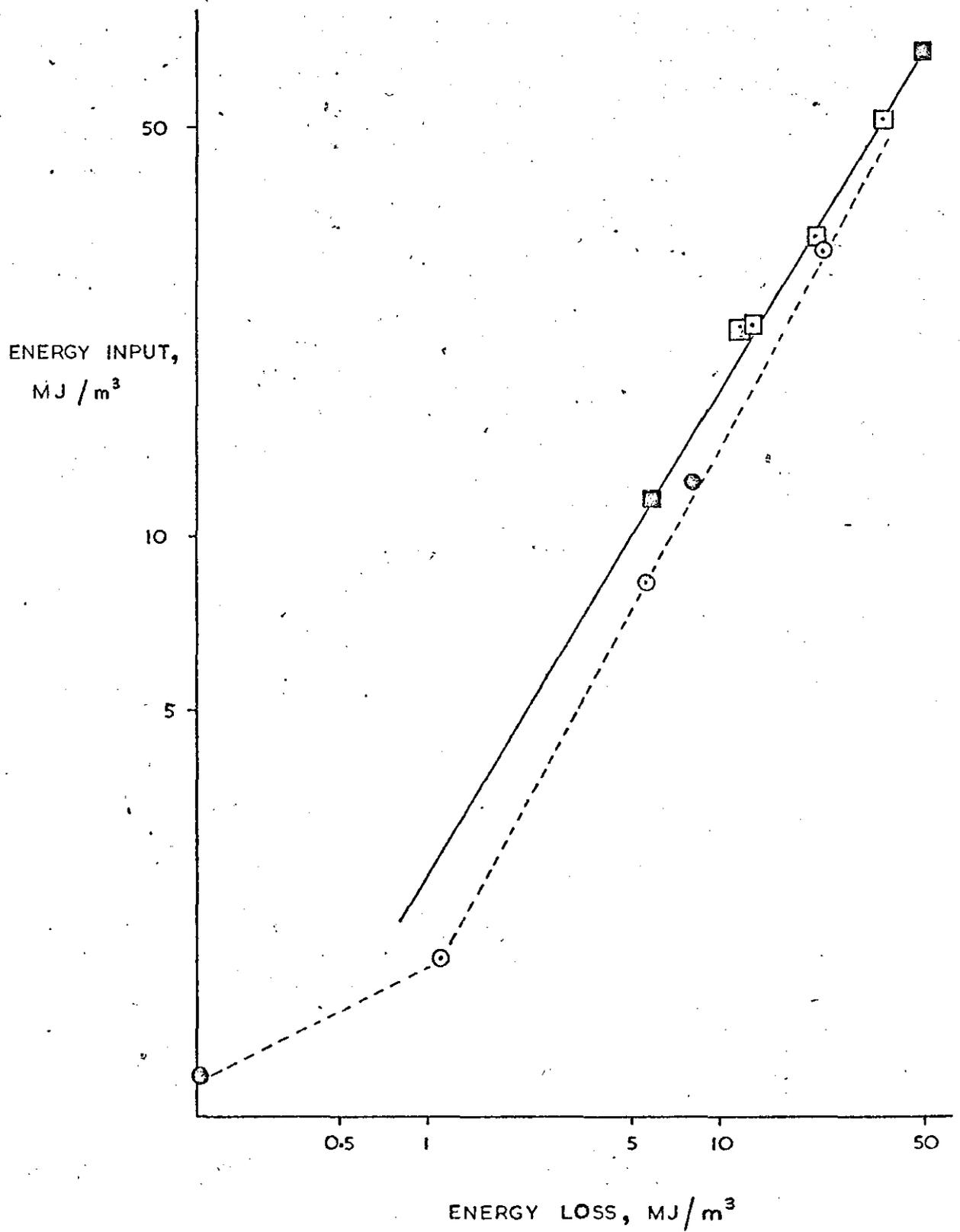


Figure 10.3 Relationship between energy input to break and energy loss to break for vulcanisates of styrene-butadiene rubber (□) and silicone rubber (○) containing 45 phr of carbon black (■) and silica (□○)

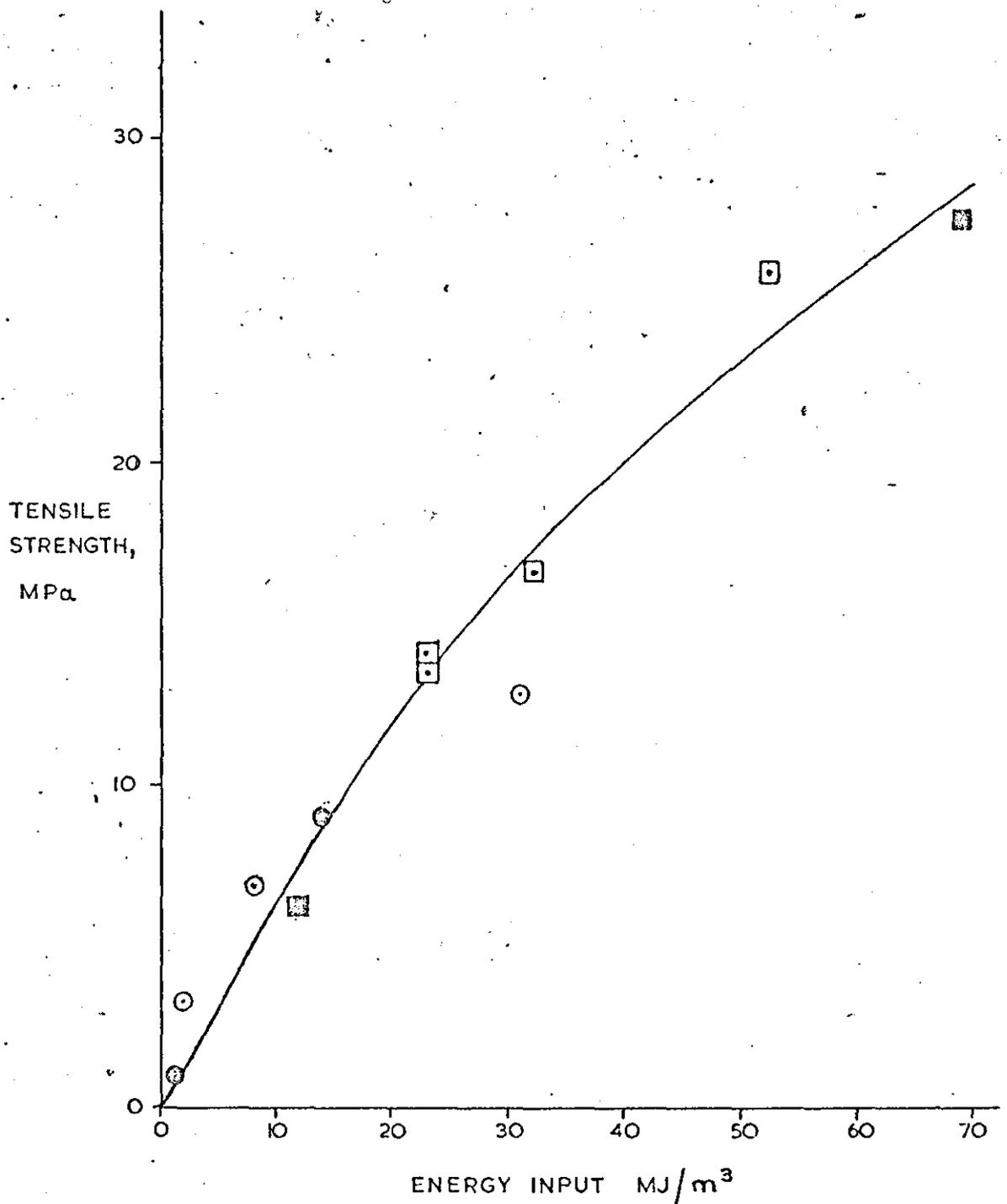


Figure 10.4 Relationship between tensile strength and energy input to break (legend as for Figure 10.3)

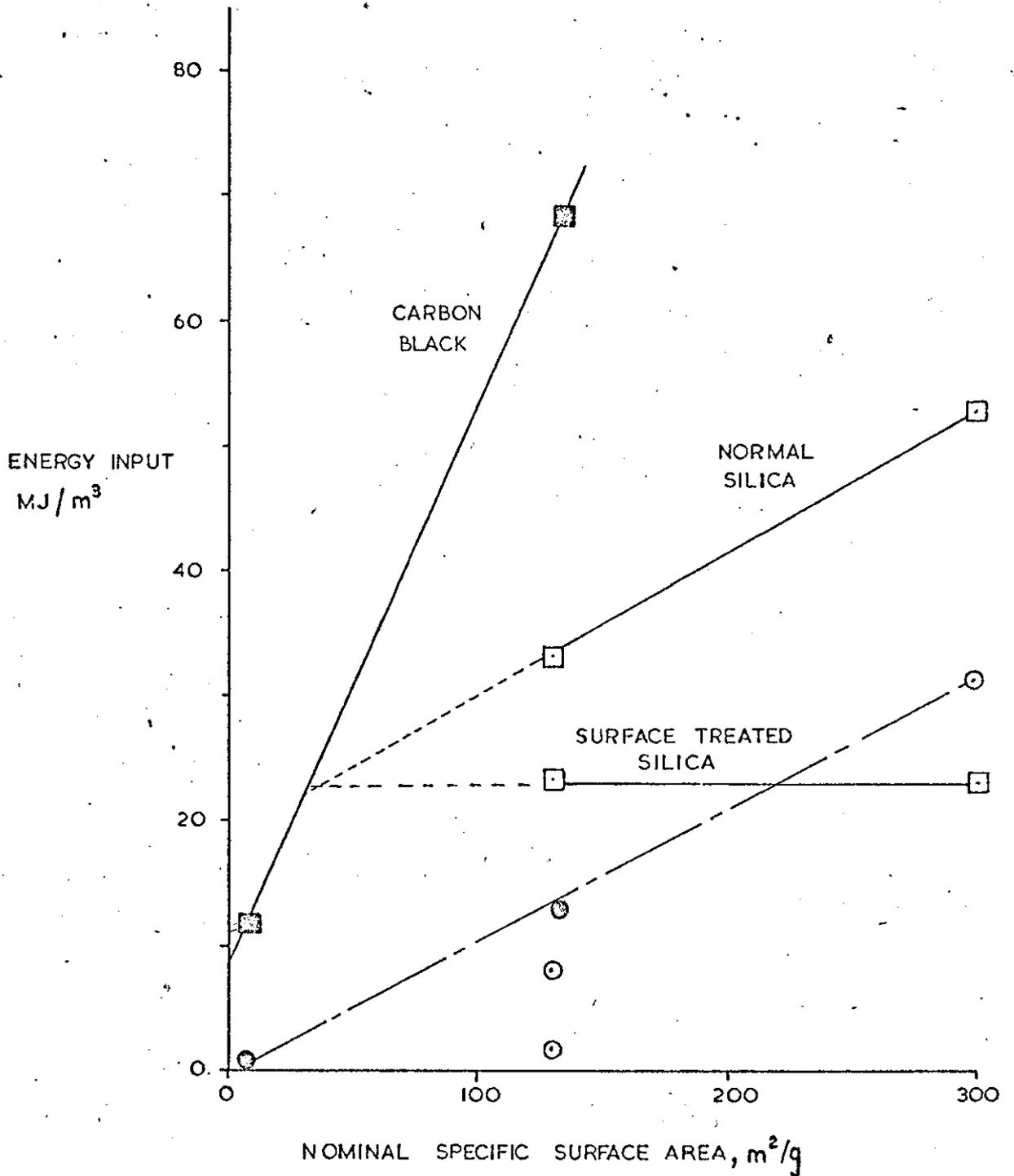


Figure 10.5 Relationship between energy input to break and nominal specific surface area of the fillers (legend as for Figure 10.3)

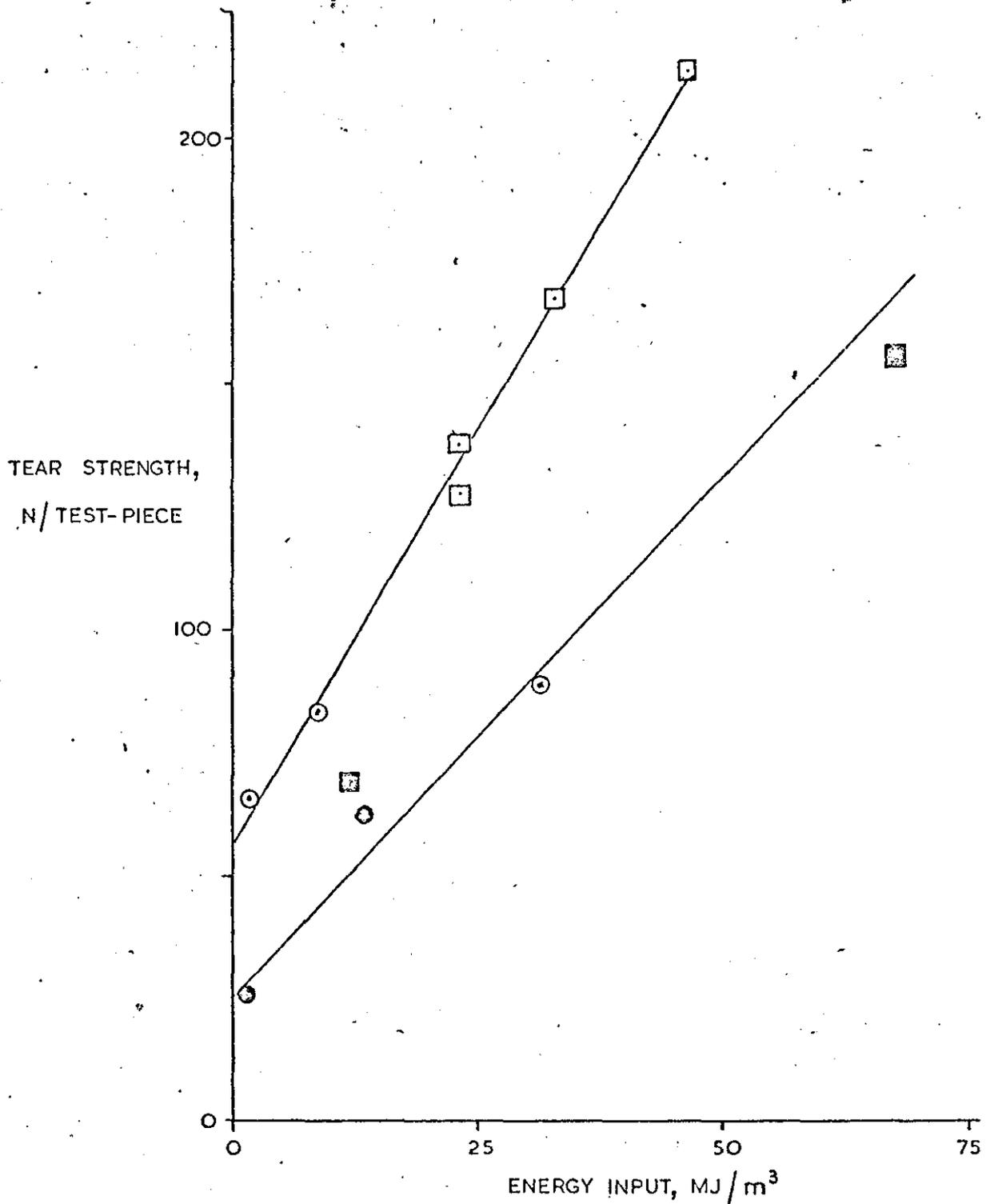


Figure 10.6 Relationships between tear strength and energy input to break (legend as for Figure 10.3)

Silicas gave very different results from carbon blacks when log (cycles to fatigue failure) was plotted against log (stored energy) (Figure 10.7); the stored energy was determined after approximately half the fatigue life. When the former was plotted against strain, however, Aerosil 300 performed similarly to HAF black, while the treated silicas performed similarly to MT black (Figure 10.8).

The results indicate that neither silica nor silicone rubber has a unique position relative to filler reinforcement of rubber; on the other hand there is no simple relationship between physical (failure) property, filler and rubber.

#### 10.2.2 Dynamic properties

E303 containing 32 phr of Aerosil 300 has been examined on the Dynamic Response Apparatus recently described (Smith and Sumner 1972).

Up to a strain of approximately 0.005 the stress-strain curve was linear and reversible. At higher strains some hysteresis was exhibited but nevertheless up to a strain of 0.02 the increasing stress portion remained linear and parallel to the lower strain curve, while much of the decreasing stress portion was also parallel to it. This effect, which was frequency independent, coupled with the onset of hysteresis coinciding with the onset of creep on "static" loading, indicated a dependence on creep rather than on a true softening, with almost immediate recovery of the original length on removal of the stress.

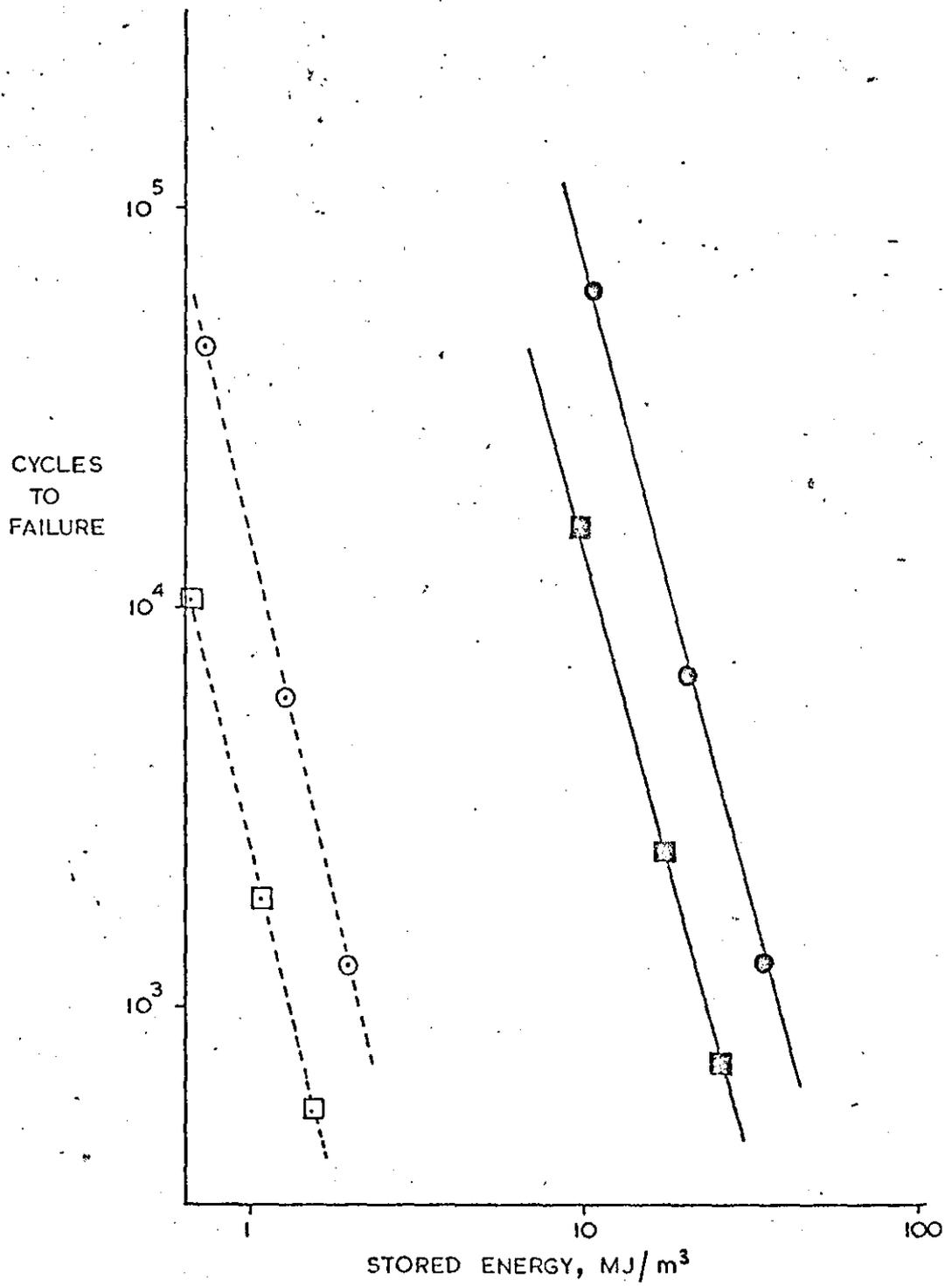


Figure 10.7 Relationship between number of cycles to fatigue failure and stored energy to break at approximately half-life, for styrene-butadiene vulcanisates containing 45 phr of filler (□

EP 154 ○ Aerosil 300 ■ MT black  
● HAF black)

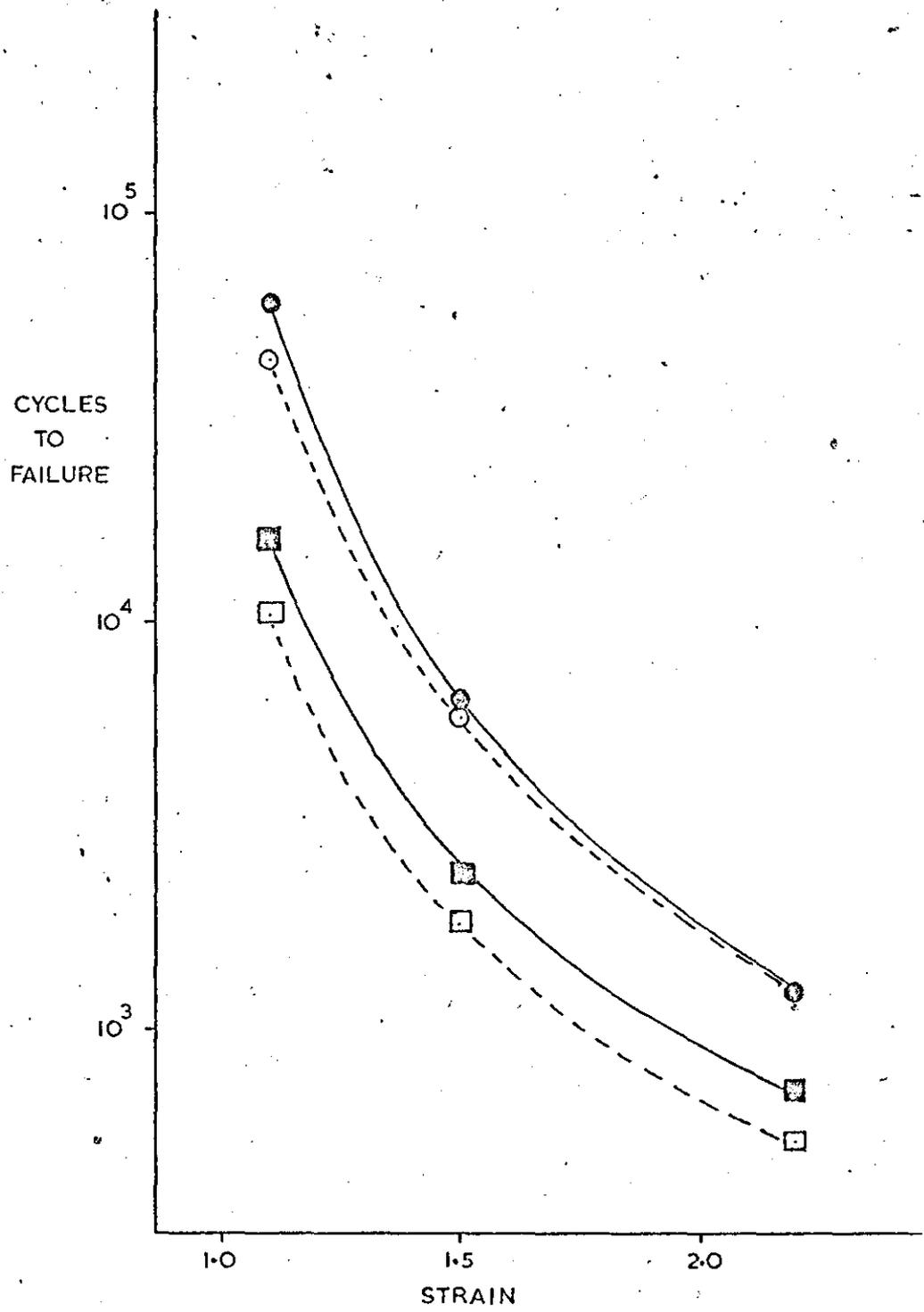


Figure 10.8 Relationship between number of cycles to fatigue failure and strain, for the vulcanisates in Figure 10.7

At much higher strains genuine softening did occur as shown by the dynamic modulus values in Figure 10.9 in comparison with those where the Aerosil 300 was replaced by EP 154. These values were obtained after cycling at highest strain to equilibrium and then reducing the strain and re-establishing equilibrium; they thus reveal some rapidly reforming structure. It was noted that the first few cycles, at 0.1, gave higher dynamic modulus but this did not occur when the determination was repeated the following day thus indicating some permanent structure breakdown. After further storage the (equilibrium) dynamic modulus was found to have increased with EP 154 but not with Aerosil 300.

It therefore appears that both reversible and irreversible structures can be broken down on deformation thus further complicating comparison of "static" and dynamic modulus. In independent work it was established that similar breakdown occurs at much higher strains if recovery is allowed to occur at a given strain before compression to slightly higher strains (Eames-Jones 1972).

Following a modification of the instrument's programme it was found possible to establish that, on the first cycle, the Young's modulus remained virtually independent of the strain to which the test-piece had been subjected previously, up to approximately 0.024. This value of Young's modulus was equal to the low strain dynamic modulus whereas the dynamic modulus at a strain of 0.024 was nearly 30% lower. This supports Payne's claim that the high value of

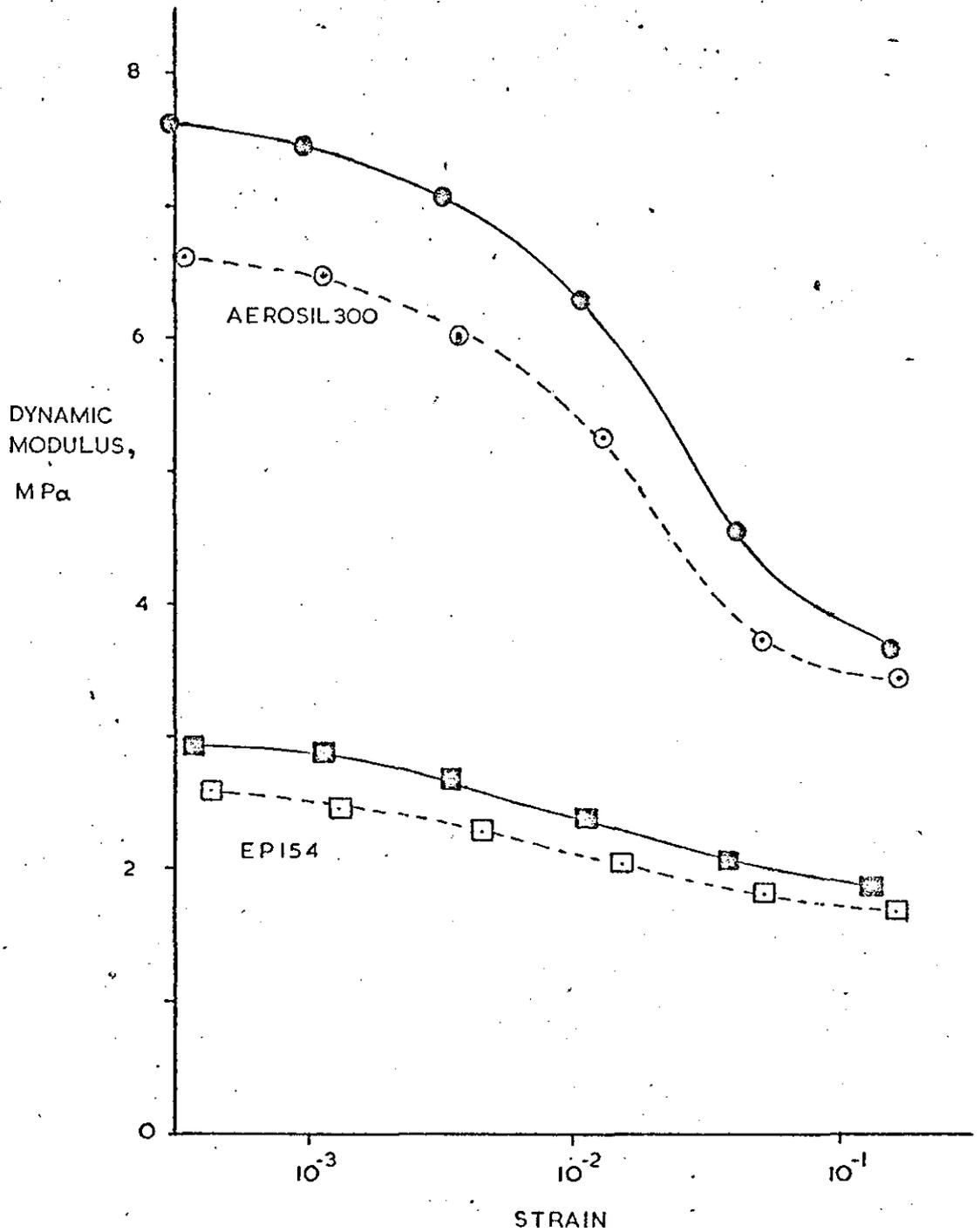


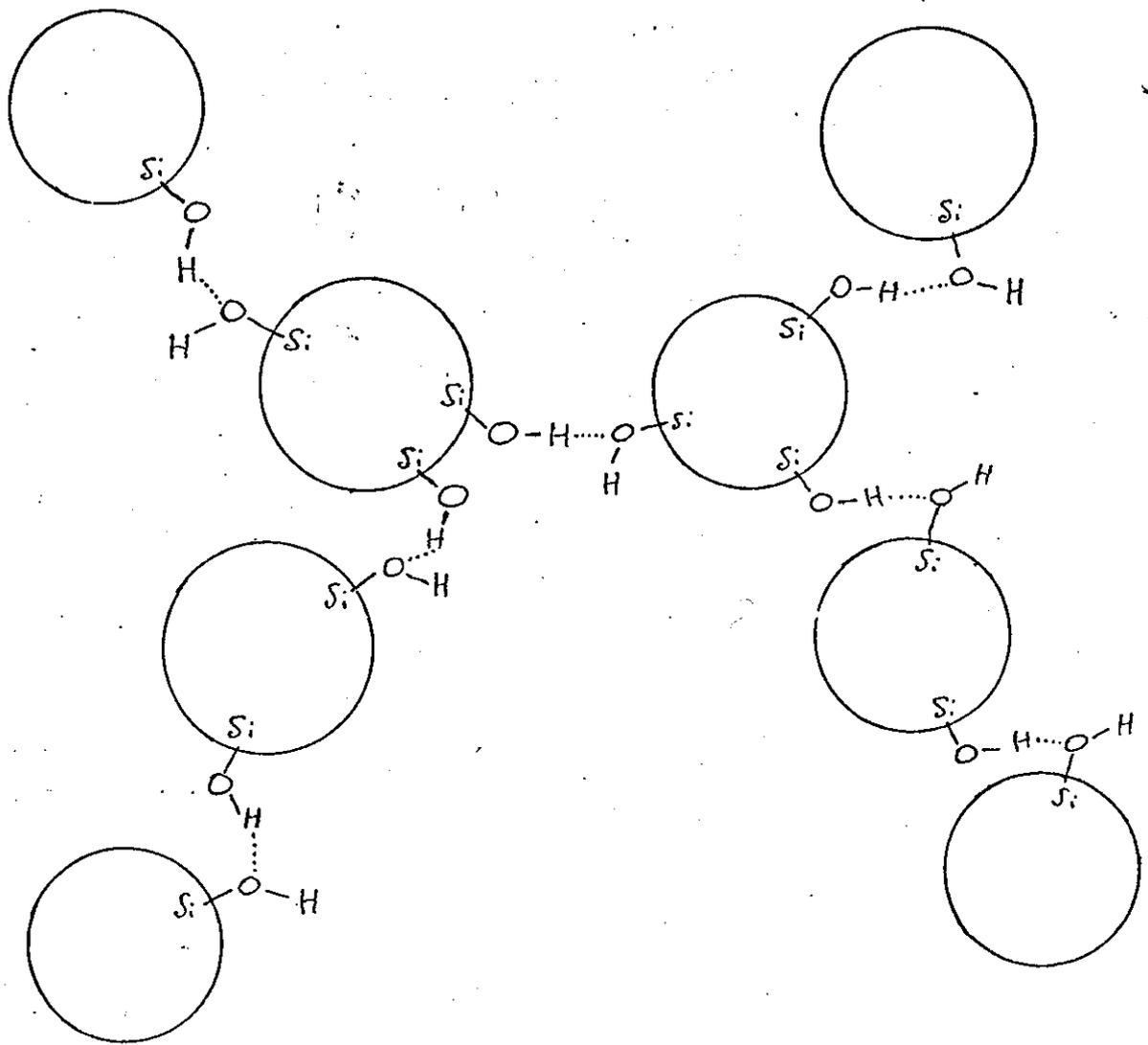
Figure 10.9 Relationship between dynamic modulus and strain for vulcanised E351 containing 32 phr of filler, determined at 1.5 Hz (□ ○) and 15 Hz (■ ●)

dynamic modulus recorded at strains below approximately 0.001 is maintained down to zero strain (Appendix 2).

## APPENDIX 2 SOME THEORIES OF REINFORCEMENT

### 11.1 INTRODUCTION

Suppliers' trade literature clearly reveals the importance of filler-filler structures in low molecular weight materials and establishes that they arise through hydrogen bonding: whereas a gel can be formed with 1-3% of a particular silica in non-polar liquids e.g. toluene, much higher concentrations are required in polar liquids e.g. 15% in ethyl alcohol, as the latter tends to hydrogen bond preferentially to the filler (Cabot 1968). Gelling can be increased by addition of short chain multi-functional hydroxyl compounds through which hydrogen bonding occurs in non-polar liquids or by addition of long chain monofunctional hydrogen bonding compounds which hydrogen bond to the filler at one end but repel a hydrogen bonding liquid at the other (Cabot 1968). The former tends to keep filler particles apart while the latter tends to do the opposite, as shown in Figures 11.1 and 11.2. Silicone oils are classed as non-polar (Cabot 1968) although the Si-O-Si bond in the polymer is polar and can readily hydrogen bond with hydroxyls; however it is different from other polar liquids in that the polysiloxane cannot hydrogen bond to itself (apart from its few hydroxyl groups) yet it can hydrogen bond to silica hydroxyls with the result that only low silica concentrations are required in silicone oil to produce a gel, as for normal non-polar liquids; indeed it may behave more like a non-polar liquid plus a multi-functional additive and other results



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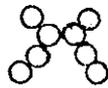


Figure 11.1 Hydrogen bonding of silica particles and method of representation in Figure 11.2

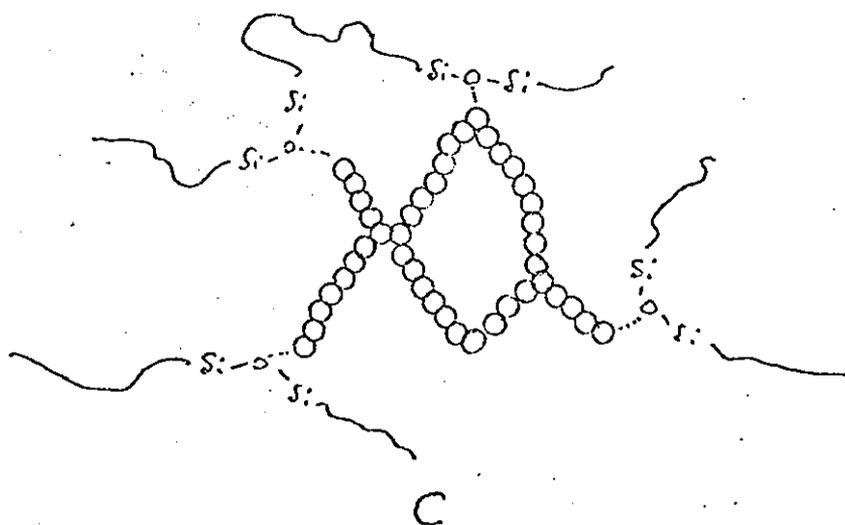
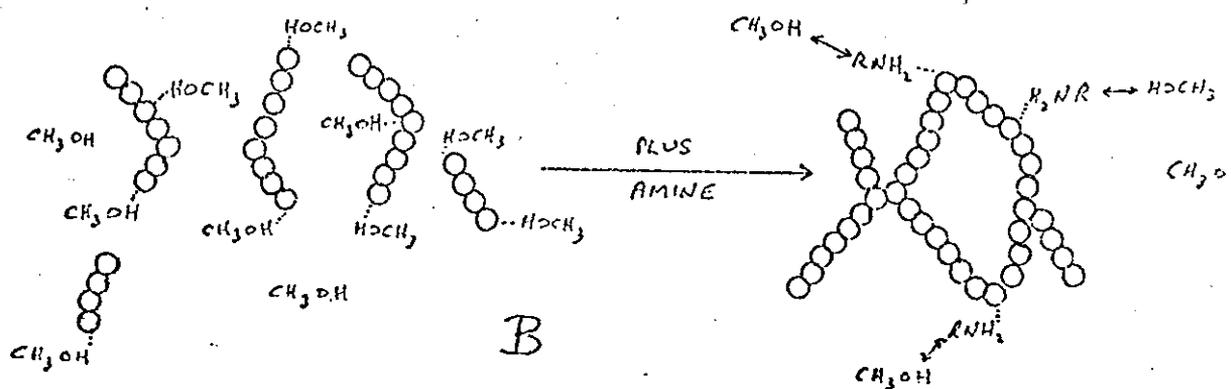
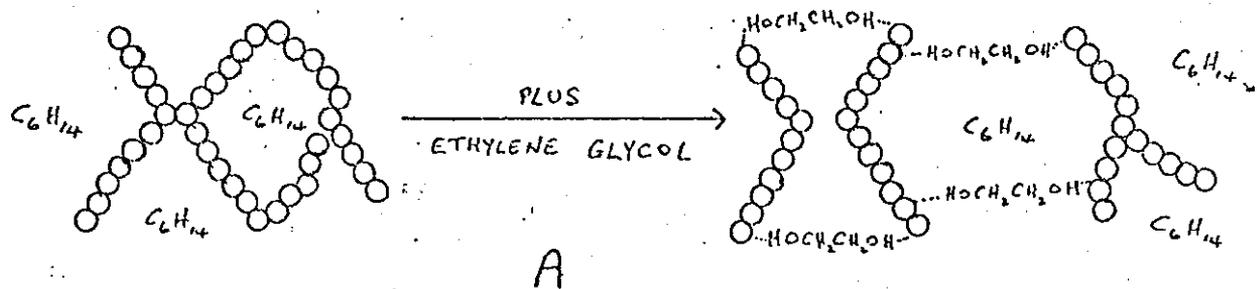


Figure 11.2 Hydrogen bonding of silica particles in various liquids

- A Non-polar (hexane)
- B Polar (methanol)
- C Polysiloxane

with Aerosil 200 did show the largest viscosity increase to be with silicone oil (Degussa).

Polysiloxanes and silicas are also claimed to undergo chemical reaction, either the siloxane bond rearrangement between polymer and filler (Patnode and Wilcock 1946) claimed by Warrick and Lauterbur (1955) or the condensation claimed by workers at Midland Silicones (1968); similar condensation, of course, occurs in the polymerisation of silanediol intermediates to silicone rubber. Such reaction would reduce the normal thixotropy of these filler-rubber mixes due to the greater stability of the chemical bonds to physical stresses.

Several workers have investigated the effect of silicas on the viscosity of silicone oil. Thomas and Moore (1972) reported very high viscosity with fine particle fume silicas, which decreased with increase of shear rate; they attributed the effects to a combination of interaction between filler aggregates and immobilisation of polymer in the vicinity of filler aggregates: with an activation energy of approximately 0.013 MJ/mol the latter was presumed to be solvation. Severn (1969) obtained similar results but in addition showed that effects were increased if the silica was first outgassed, and decreased if the silica was reacted with methanol.

Pocknell, Thomas and Kendrick (1969) examined similar systems but also showed that viscosity increased to its original value on decreasing the shear rate; however, on

standing, the oil containing Aerosils "aged" and subsequently showed less shear rate dependence; the activation energy of the "ageing" reaction was approximately 0.03 MJ/mol: both effects were concluded to involve physical rather than chemical changes and the latter was attributed to a polar interaction between silica hydroxyls and polymer siloxane bonds. They also reported an almost constant activation energy of viscous flow (approximately 0.015 MJ/mol) irrespective of filler, indicating that the filler did not materially affect the polymer mobility. They concluded that the viscosity effects were due to asymmetry of filler aggregates and to polymer-filler interaction, plus interaction between untreated filler aggregates until they were "broken" by solvation during "ageing".

In a low molecular weight polysiloxane it appears that polymer hydrogen bonds to aggregates of a filler such as Aerosil 300 but that the mix can still be fully thixotropic. However, on standing there is some further polymer-filler interaction, again physical in nature, which can reduce or eliminate the filler-filler interaction by "protecting" the filler - this is equivalent to the author's adsorbed rubber: these two stages probably only differ in the amount of hydrogen bonded rubber. With surface treated filler analogous to EP 154 Pocknell, Thomas and Kendrick (1969) only observed filler asymmetry effects.

Increase of molecular weight of the polymer has the effect of increasing the activation energy of the polymer-filler interaction to the approximately 0.08 MJ/mol reported by Wagner and Sellers (Section 1.3) and by Kraus and Dugone (1955), thus implying chemisorption. However, many systems have given lower values, and many workers have reported inconclusive evidence. Sircar and Voet (1970) dismissed the multicontact adsorption theory of Frisch, Simha and Eirich (1953) except perhaps at high black concentrations in milled rubber. From the dependence of extracted rubber on solvent type and temperature they concluded that at least some of the polymer was chemisorbed, with a spectrum of bonding energies.

Berry and Cayré (1960) obtained an activation energy of approximately 0.08 MJ/mol with samples heated without milling; this was attributed to energy of production of free radicals. An activation energy of only approximately 0.04 MJ/mol for adsorption following milling was attributed to the interaction being dependent on the diffusion rate of polymeric free radicals.

There is undoubtedly a dependence on various factors and it is not surprising that published literature remains confused so that Blow (1973) was not able to draw conclusions on this aspect in his bound rubber review. The question has recently been argued in the Central Criminal Court with respect to a low molecular weight polysiloxane and Aerosil 200; no ruling was given on the type of adsorption but the side claiming chemisorption

lost its case through inability to prove it "beyond any reasonable doubt" (Burton 1972).

There is however no doubt about the existence of filler-filler structures in rubbers as well as in liquids thanks to the classical work of Payne: that these exist in the silicone rubber-silica system is established in Appendix 1. Voet, Cook and Hogue (1970) showed how transient carbon black structures increased as diluent was removed from preswollen vulcanisates to decrease the interparticle (black) distances: transient structure refers to that which arises from mutual attraction of filler aggregates (persistent structure) by van der Waals forces and which is broken down by increasing strain amplitude. Persistent structure refers to the strong attachment between individual filler particles (at least for carbon black) to produce an aggregate whose asymmetry may be important (Section 11.2).

## 11.2 REINFORCEMENT EQUATIONS

Guth (1945, 1948) showed that the Young's modulus ( $E$ ) of a rubber vulcanisate containing thermal carbon black was related to the Young's modulus ( $E_0$ ) of the gum vulcanisate by the expression:-

$$E = E_0 (1 + 2.5c + 14.1c^2) \quad \dots (2)$$

for values of  $c$ , the volume concentration of filler, up to approximately 0.2.

He found equation (2) inadequate for smaller particle size carbon blacks and proposed a second expression:-

$$E = E_0 (1 + 0.67fc + 1.62f^2c^2) \dots (5)$$

where  $f$  was a shape factor describing the asymmetric nature of filler aggregates as expressed by the ratio of their length to width but which decreased on repeated extension and relaxation of test-pieces. He emphasised that these equations applied to mixes in which only Van der Waals type forces maintained rubber-filler adhesion and postulated higher values for the coefficients in the presence of chemical bonding.

Mullins and Tobin (1965) confirmed the validity of equation (2) for medium thermal black for volume concentrations up to approximately 0.2 using Young's modulus obtained from stress-strain curves linear up to strains of approximately 0.02. They also obtained good agreement with equation (5) for high abrasion furnace black for volume concentrations up to approximately 0.15 using a value of  $f = 6.5$  chosen to give the best fit to the experimental values. Other workers have used similar values of  $f$  and claimed close correspondence with values observed in electron micrographs (Cohan 1947).

On the other hand Bueche (1957) determined the modulus of silicone rubber at strains of approximately 0.4 and required values of  $f$  ranging from 10 for a semi-reinforcing

silica to 116 for a highly reinforcing silica; these values were considered to be unrealistic following examination of electron micrographs.

Vandenberg, Ralston and Kocher (1969), working with vulcanisates of natural rubber and polyepichlorhydrin rubber found that Young's modulus on first extension indicated asymmetry for both fast extrusion furnace black and silica, with values of  $f = 5.5$  and  $12$  respectively in equation (5): on fifth extension (to maximum stress?) the Young's modulus in the presence of the former gave good agreement with equation (2) while that with the latter gave good agreement with equation (5) with the lower value of  $f = 5$ .

Brennan, Jermyn and Boonstra (1964) had some success when they replaced  $c$  in equation (2) by a reinforcement volume  $\phi$ , being the sum of the volume concentration of carbon black and its bound (polybutadiene) rubber. For Mooney viscosity they used the expression:-

$$M = M_0 (1 + 2.5\phi + 14.1\phi^2) \quad . . . . (7)$$

Later Brennan and Jermyn (1965) obtained good agreement with equation (7) and stress at a strain of 3.0 but not with stress at 0.25 strain where they concluded that carbon black agglomerates were the dominant factor.

Grosch (1968) determined the breaking stress of swollen vulcanisates and found that the limiting values, as solvent concentration was increased, fitted equation (5)

with  $6 < f < 7$ . However examination of shift factors required to produce master curves and comparison with glass transition temperatures indicated non-uniformity of polymer effect in filled vulcanisates which he concluded could be due to a shell of rubber around the filler particles.

Various workers have proposed that enhancement of modulus etc. is due to an increase in elastically effective polymer chains through polymer-filler interaction (Bueche 1957; Payne 1965) but there has been a recent trend to attribute some of the effect to restricted motion of polymer in the region of filler particles (Harwood, Payne and Whittaker 1969).

It is still generally accepted that the decrease in dynamic modulus on increase of strain, as demonstrated by Payne (1965), is due to the breakdown of filler-filler agglomerates but there remains the apparent anomaly that, using values of  $f$  in the region of 6.5, approximate agreement with equation (5) for a high abrasion furnace black was obtained at effectively zero strain in static measurements (Mullins and Tobin 1965) but only at strains ( $> 0.5$ ) sufficient to break down the agglomerates in dynamic measurements (Payne 1965). Although Voet and Aboytes (1970) have reported a decrease in dynamic modulus at very low strains ( $< 0.05$ ) Payne considered that it was an instrumental artefact (1971).

This decrease, attributed to breakdown of filler-filler agglomerates, is reduced by improved dispersion, by hot milling and by attrition of the filler etc.

(Payne 1965) although no explanation appears to have been given. Presumably these treatments reduce the tendency for filler aggregates to agglomerate.

Brennan (1974) may be partially correct in his suggestion that the decrease in stress is due to a reduction in the molecular weight of the rubber and indeed some of the results of Voet, Aboytes and Marsh (1969) showed that intensive milling reduced dynamic modulus at relatively high strains. Medalia (1972) has recently reviewed evidence that shape factors of approximately 6 are not acceptable for a high abrasion furnace black; more realistic values are about 1.8 and do not give good agreement with equation (5).

Medalia (1970) proposed that some rubber is immobilised by occlusion in filler aggregates, dependent on filler structure as revealed by absorption of dibutyl phthalate etc. Sambrook (1970) applied this to a further modification of equation (2) with  $c$  replaced by  $\phi_1$ , being the sum of the volume concentration of carbon black and its occluded rubber:-

$$E = E_0 (1 + 2.5\phi_1 + 14.1\phi_1^2) \quad \dots \quad (8)$$

He found that  $\phi_1$ , determined from the dibutyl phthalate absorption, was an overestimate and he attributed this to deformation of some of the occluded rubber on extension

of his test-piece. Medalia (1972) subsequently reported an occluded volume effectiveness factor of approximately 0.5. He claimed equation (8) was preferable to equation (4) as the latter would fail to predict a difference in modulus with two carbon blacks of equal particle size but different structure which he further claimed would have constant bound rubber; however his own limited values showed an increase in bound rubber with increase in structure (1973 2). Dannenberg (1966) established a linear relationship between bound rubber and dibutyl phthalate absorption.

Brennan (1971) proposed that bound rubber could not absorb curatives during mixing, with the result that the rest of the rubber had a higher curative concentration: he claimed that this accounted for the apparent increase in crosslink density in a vulcanisate containing reinforcing filler. Medalia (1973 1) does not accept this possibility but perhaps he would if the bound rubber was actually occluded.

It is sometimes overlooked in application of Guth-Gold type equations that these only hold for filler volume concentrations up to approximately 0.2; concentrations often exceeded in practical rubber-filler mixes, particularly if bound rubber or occluded rubber is treated as part of the filler. It is then necessary to consider the various adaptations for high concentrations of filler,

particularly those of van der Poel (1958) who allowed for modulus differences between filler and matrix, and Oberth (1967) who collected values from other investigations. Baker, Charlesby and Morris (1968) concluded that reinforcement was a physical effect, at least at high strains, but they failed to allow for the van der Poel enhancement in the presence of high concentrations of filler.

Brennan (1971) may be correct in stating that bound rubber and/or occluded rubber does not absorb curatives but it is not relevant to the properties of unvulcanised mixes of rubber and filler: for such mixes there still appears to be no one theory to explain sufficient of the values observed with rubber containing carbon blacks more "reinforcing" than thermal blacks. It appears that filler-filler structures may be mainly responsible for the deviations from the various theoretical expressions: as such structures are likely to affect the bound rubber, either directly or indirectly, it is not surprising that sometimes "reinforcement" has been successfully correlated with bound rubber.

### 11.3 STRESS-STRAIN RELATIONSHIPS

Young's modulus is by definition determined at the very low strains where stress is proportional to strain. Such Hookean behaviour is not generally accepted for rubber and indeed may only be apparent because other

expressions tend towards this simple case at low strains. Although an individual polymer chain can be considered to exhibit Hookean behaviour by fixing its ends at specified points this is not practical and therefore elasticity has to be considered as arising from a statistical or Gaussian distribution, according to the kinetic theory equation:-

$$\sigma = \nu k T (\lambda - \lambda^{-2}) \quad \dots (9)$$

where  $\sigma$  is the tensile stress,  $\lambda$  the extension ratio,  $k$  the Boltzmann constant,  $T$  the absolute temperature and  $\nu$  the number of effective network chains per unit volume.

Various assumptions are made including:-

- (a) there is no volume change on deformation
- (b) deformation is affine
- (c) there is no appreciable internal energy change
- (d) extension is not too great.

Bueche (1957) applied this to his silica filled silicone rubber vulcanisates, when equation (5) was found unsuitable, assuming equivalence of polymer-polymer crosslinks and polymer-filler attachments. He used the expression:-

$$\frac{\sigma}{\nu k T V_1 (\lambda - \lambda^{-2})} = \nu_0 + \beta \frac{V_2}{V_1} \quad \dots (10)$$

where  $\nu_0$  applied to the gum vulcanisate and  $V_1$  and  $V_2$  were the volume fraction of rubber and filler respectively. He obtained straight lines which enabled him to calculate that the area of filler surface per polymer attachment ranged from 0.2 to  $4 \text{ nm}^2$  dependent on filler.

Normally equation (9) does not adequately represent the behaviour of rubber vulcanisates, even in the absence of filler, and it is necessary to invoke the Mooney-Rivlin expression derived from the phenomenological theory of large elastic deformations and incorporating two constants  $C_1$  and  $C_2$ :-

$$\frac{\sigma}{(\lambda - \lambda^{-2})} = 2C_1 + \frac{2C_2}{\lambda} \quad \dots \dots (11)$$

This only reverts to equation (9) when  $2C_1 = \nu kT$  and  $2C_2 = 0$ ; the latter is believed to represent equilibrium conditions and can be achieved following immersion in a good solvent; it may also apply in a rubber with very flexible chains e.g. silicone rubber which at room temperature is well above its glass transition temperature.

Sato and Furukawa (1962) have adopted a different approach but the net result, for bonded fillers, reduces to a form similar to that of equation (10).

#### 11.4 IMMERSION IN LIQUIDS

In his review of the diffusion of liquids in elastomers, van Amerongen (1964) showed that the amount of liquid absorbed by a sheet of vulcanised rubber is proportional to the square root of the immersion time, until at least half the equilibrium quantity has been absorbed: a similar relationship held for desorption of liquid. More recently

Southern and Thomas (1967) and Blow, Exley and Southwart (1968) have reported similar behaviour for a range of liquids and rubber vulcanisates.

The volume fraction of rubber ( $V_{2m}$ ) in a vulcanisate swollen to equilibrium can be used to determine the effective number of crosslinked units by substitution in the Flory-Rehner equation:-

$$\ln(1-V_{2m}) + V_{2m} + \chi_1 V_{2m}^2 = - \frac{\rho V_1}{M_c} \left(1 - \frac{2M_c}{M}\right) \left(V_{2m}^{\frac{1}{3}} - \frac{V_{2m}}{2}\right) \dots \dots (12)$$

$M$  and  $\rho$  are the molecular weight and density of the uncrosslinked polymer,  $M_c$  is the molecular weight per crosslinked unit and  $\chi_1$  is the polymer-solvent interaction parameter.

The derivation of the equation and its application to unvulcanised silicone rubber-silica mixes were reported earlier (Southwart 1969 2): the work included an examination of the changes in a swollen gel when it was immersed in a solution of the same polymer. Solvent was desorbed from the gel because of the difference in solvent activity in gel and solution. The phenomenon is partially dependent on the osmotic pressure of the solution and has been described as an "osmotic pressure effect" or "back pressure effect": besides decreasing the solvent content of the gel it also increases the observed bound rubber. Recently Blow (1973) has reanalysed some of the

results in terms of a partition coefficient (P).

In a mixture of 100 parts (weight) of rubber and F parts (weight) of filler he denoted the (true) bound rubber as B, and the soluble rubber as  $S_g$ . At equilibrium, following immersion in  $T_1$  parts of a solvent containing  $S_s$  parts of dissolved rubber, the gel contained  $S_g'$  parts of soluble polymer and  $T_2$  parts of solvent, while the solution contained  $S_s'$  parts of polymer in  $T_3$  parts of solvent. The partition coefficient P, being the ratio of soluble rubber concentration in the gel to that in the solution, was equal to  $S_g' T_3 / S_s' T_2$  and was related to the (true) bound rubber B and the observed bound rubber G by the expression:-

$$G = P S_s' T_2 / T_3 + B \quad \dots \dots (13)$$

A plot of G against  $S_s' T_2 / T_3$  gave a straight line of slope P and intercept B.

There is extensive literature on the subject, particularly on the application of the Flory-Rehner equation to vulcanisates but considerable doubt remains on the interpretation of the results in the presence of reinforcing fillers. Blanchard (1973), for example, has recently published further equations in his continuing attempt to interrelate the various changes occurring when a vulcanisate is immersed in a liquid.

APPENDIX 3 DETERMINATION OF SURFACE AREA OF SILICA  
BY TITRATION

<u>Solutions required</u>	Buffer solutions pH 4    pH 9
	O.1 N Standard sodium hydroxide
	Dilute hydrochloric acid
	Sodium chloride (R) solution (200 g made up to 1 l with deionised water)

Method

- i) Check zero of Model 38B pH meter.
- ii) Switch on meter and leave for 5 minutes minimum.
- iii) Immerse electrodes in buffer solution pH = 9, switch to pH AUTOMATIC 6-14 and set BUFFER/MV ZERO to read correctly for precise pH, dependent on solution temperature.
- iv) Switch to "check" and note meter reading on top scale.
- v) Wash electrodes and transfer to buffer solution pH = 4. Set to pH AUTOMATIC 0-8, record reading. Switch to "check". Wash electrodes and transfer to deionised water.
- vi) Add approx. 20 ml silica to small beaker and weigh (approx. 34.4 g), transfer to 250 ml graduated beaker and reweigh small beaker: calculate difference in weight.
- vii) To beaker containing silica add plastic covered magnet and 100 ml sodium chloride solution; immerse electrodes and make up solution to 150 ml approx; set stirrer control to 5.

- viii) Switch to pH AUTOMATIC 0-8, note reading, add few drops of dilute hydrochloric acid to reduce reading to just below pH = 4.0. Add standard sodium hydroxide solution from burette until pH = 4.0, note burette reading.
- ix) Start laboratory clock; titrate to pH = 9 approx. (changing to pH automatic 6-14 where appropriate) as rapidly as possible (within 20 seconds of starting clock); maintain meter reading at pH = 9.0 by further additions as required.
- x) After two minutes wash electrodes etc., continue titration and note burette reading after 5 minutes (total).
- xi) Switch pH meter to CHECK, stop stirrer motor, remove electrodes, wash and transfer to deionised water; calculate volume of sodium hydroxide solution added.
- xii) Calculate specific surface area =

$$\frac{32 \times \text{volume of sodium hydroxide added (ml)}}{\text{weight of filler (g)}} - 25$$

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EQUATIONS

(1) $S = 32 V - 25$	25 246
(2) $E = E_0 (1 + 2.5c + 14.1c^2)$	131 132 143
	144 146 149
	150 151 196
	<u>234</u>
(3) $D = (\pi/6c)^{\frac{3}{2}} d - d$	194
(4) $E = E_0 (1 + 2.5\phi + 14.1\phi^2)$	196 197 199
(5) $E = E_0 (1 + 0.67fc + 1.62f^2c^2)$	198 200 <u>235</u>
(6) $E = E_0 (1 + 0.67f,\phi + 1.62f,^2\phi^2)$	198 200
(7) $M = M_0 (1 + 2.5\phi + 14.1\phi^2)$	236
(8) $E = E_0 (1 + 2.5\phi_f + 14.1\phi_f^2)$	238
(9) $\sigma = \nu k T (\lambda - \lambda^{-2})$	241
(10) $\frac{\sigma}{\nu k T V_1 (\lambda - \lambda^{-2})} = \nu_0 + \beta \frac{V_2}{V_1}$	241
(11) $\frac{\sigma}{(\lambda - \lambda^{-2})} = 2 C_1 + \frac{2 C_2}{\lambda}$	242
(12) $\ln(1 - V_{2m}) + V_{2m} + \chi_1 V_{2m}^2 = -\frac{\rho V_1}{M_c} \left(1 - \frac{2M_c}{M}\right) \left(V_{2m}^{\frac{1}{3}} - \frac{V_{2m}}{2}\right)$	243
(13) $G = PS_s' T_2/T_3 + B$	244

Symbols are defined with the equation in which they are first used, or on the page underlined above in cases of multiple references, except that  $\beta$  in equation (10) is a proportionality constant.