EFFECT OF FEEDING RATE IN POLYMER EXTRUSION

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P. J. JOSEPH FRANCIS

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COCHIN - 682 022

APRIL 1998

ASPIRATION…

PERSPIRATION……..

AND THEN

PRECIPITATION.

TO

MY PARENTS

&

PARENTS IN LAW

CERTIFICATE

This is to certify that this thesis entitled "Effect of Feeding Rate in Polymer Extrusion " is an authentic record of the research work carried out by Mr. Joseph Francis. P.J. under my supervision and guidance in the Department of Polymer Science and Rubber Technology. No part of the work reported in this thesis has been presented for any other degree or diploma from any other institution earlier.

Rani Joseph

Prof.(Dr.) Rani Joseph
(Supervising Teacher)
Professor, Department of Polymer
Science and Rubber Technology
Cochin University of
Science and Technology

Kochi 682022

20th April 1998

DECLARATION

I hereby declare that the thesis entitled "Effect of Feeding Rate in Polymer Extrusion" is an authentic record of the research work carried out by me under the supervision of Prof.(Dr.) Rani Joseph, Professor, Department of Polymer Science and Rubber Technology, Cochin University of Science and Technology, Kochi 682022, and no part of the work reported in this thesis has been presented for any other degree or diploma from any other institution earlier.

P. J. Joseph Francis

Joseph Francis, P.J.

Kochi 682022

20th April 1998

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JOSEPH FRANCIS.

LIST OF ABBREVIATIONS

POLYMERS

IIR	Isobutylene–isoprene rubber
LDPE	Low density polyethylene
NR	Natural rubber
PS	Polystyrene
SBR	Styrene–butadiene rubber

ADDITIVES

CBS	N–cyclohexyl–2–benzthiazyl sulphenamide
HAF	High abrasion furnace black
MBTS	Dibenzthiazyl disulphide
S	Sulphur
TMTD	Tetramethyl thiuram disulphide
ZnO	Zinc oxide

OTHER ABBREVIATIONS

ASTM	American society for testing and materials
BS	British standards
cc	Cubic centimetre
DSC	Differential scanning calorimetry

E	Eccentricity factor of the screw
e	Flight width
gm	Gram
H	Channel depth
ISNR	Indian standard natural rubber
K	Shape dependent factor
L	Effective screw length
M_c	Number average molecular weight
m_f	Weight of the filler
mg	Milligram
min	Minute
ML(1+4) at 100°C	Mooney viscosity determined using large rotor after a dwell time of one minute and rotor run of four minutes at 100°C.
m_p	Weight of the polymer
MPa	Mega Pascal
N	Screw speed
Nm	Newton meter
N/mm^2	Newton per millimetre square
P	Head pressure
phr	Parts per hundred rubber
ΔP	Overall pressure drop along the screw
$\frac{dP}{dL}$	Pressure gradient
$Q_{max.}$	Maximum output

Q_d	Drag flow
Q_l	Leakage flow
Q_p	Pressure flow
rpm	Revolutions per minute
R_B	Percentage bound rubber content
SEM	Scanning electron microscope
TGA	Thermogravimetric analysis
t_{90}	Optimum cure time
UTM	Universal testing machine
VGC	Viscosity gravity constant
V_r	Volume fraction of rubber in the network
V_s	Molar volume of the solvent
W	Weight of the specimen
W_{fg}	Weight of the carbon black and gel
z	Weight fraction of filler
δ	Clearance space
η	Fluid viscosity
ρ_r	Density of rubber
ρ_s	Density of solvent
ϕ	Helix angle

CONTENTS

CHAPTER 1

INTRODUCTION

INTRODUCTION

Among the different types of polymer processing operations such as extrusion, mixing, melt spinning, film blowing, coating, calendering, compression moulding, injection moulding, blow moulding, thermoforming etc., extrusion and injection moulding are the most widely used. Also, in the most modern injection moulding machines, the preparation of melt for injection is carried out in what is essentially a screw extruder. Similarly blow moulding and calendering are often post-extrusion operations.

Since extrusion is the basis of most other processing techniques and with over one half of all polymeric materials being processed in this manner understanding its operation is extremely important.[1] Many comprehensive literature[2–15] and books[16–22] have been written on extrusion. Fundamentally the process of extrusion consists of converting a suitable raw material into a product of specific cross section by forcing the softened material through an orifice or die under controlled conditions. Most of the thermoplastics and elastomers pass through an extruder at least once during their lives; if not during fabrication of the end product, then during the homogenization stage. Among the products, manufactured by extrusion are pipe, rod, film, sheet, fiber, unlimited number of shapes or profiles and other ~~non~~-continuous products.

1.1 SCREW EXTRUSION

1.1.1 Basic principles

Fundamentally, the screw extrusion machine consists of a screw of special form rotating in a heated barrel or cylinder in which a feed opening is placed radially or tangentially at one end and an orifice or die axially at the other. A restriction in the form of a breaker plate is sometimes placed between the end of the screw and the extruding die in order to assist build up of a pressure gradient along the screw. Recent techniques have indicated that control of pressure at the die is important and a valve is sometimes used in addition to a breaker plate and screen. The screw is usually bored throughout or for some part of its length, so that it may be fluid cooled or heated, according to the requirements of the feed material.

The rotating screw takes the material which is usually in the form of a free flowing cold chips, powders, cubes, sheets or strips from the feed opening or feed roll through the heated barrel zones, and compacts it against the breaker plate or other restriction, so that a pressure is built up. During this period, the material is forced into intimate and substantially sliding contact with the hot barrel walls and is also sheared and worked so that frictional effects are produced.[23] The combined effects of the hot barrel and the heat due to internal friction in the material cause the polymer to soften so that it may be forced through the

restriction to the extrusion die where it is given the required form.[24] Figure 1.1 shows a simplified sketch of a screw extruder.

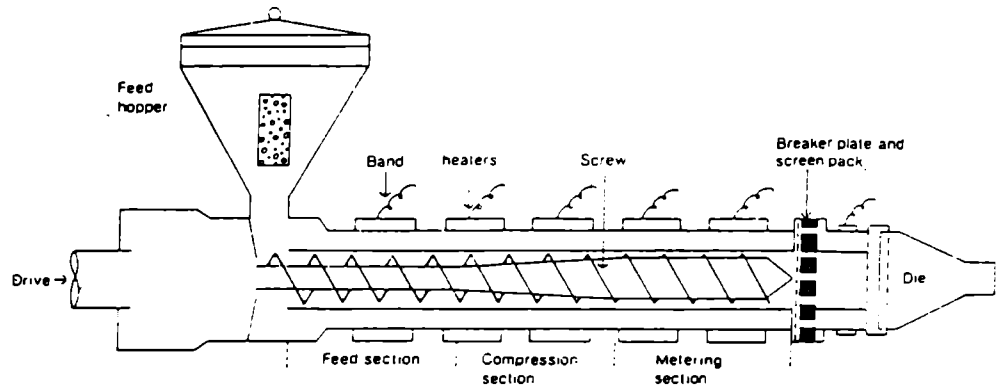

Fig.1.1 A screw extruder

1.1.2 Extruder screw

The single most important element of a screw extruder is the screw. Extruder screws as a general rule employ simple-start flights although two or even more starts are sometimes used. The alteration of flight depth to obtain a compression on the material as it moves towards the die is standard practice on most screws and is either carried out progressively throughout the length of the screw, or in stages, or by a combination of both methods. The deliberate reduction of the volumetric capacity of the screw channel or channels is necessary in order to accommodate the reduction in volume of the material as it becomes fluid and homogeneous and to apply compression to the material so that the channel is completely filled. The typical screw of a conventional

thermoplastic extruder and a rubber extruder is shown in the figures 1.2a and 1.2b.

Fig.1.2a Screw of a conventional thermoplastic extruder

Fig.1.2b Screw of a conventional rubber extruder

1.1.3 Diameter and length of the screw

If the screw is considered solely as a means of conveying the material, then the diameter and length are major factors in determining its volumetric capacity and hence the quantity of feed material can handle. These two functions remains important controls of capacity irrespective of screw design. The length and diameter have a second important influence in that they affect the rate at which heat is transferred from the barrel walls to the material, and this in turn affects the amount of heat generated by friction and shear, the energy input and the power to throughput ratio.

1.1.4 General screw design

The proper design of the geometry of the extruder screw is of crucial importance to the proper functioning of the extruder. One of the important requirements for screw design is that the screws have sufficient mechanical strength to withstand the stresses imposed by the conveying process in the extruder. The important factors are the following.

a) Pitch of the screw thread and the speed of the screw

The reduction of the volumetric capacity can be obtained by progressively reducing the pitch of the flights without changing their depth or by a combination of both methods. The pitch of the flight is, in conjunction with the peripheral speed, one of the major factors determining the output of the machine. It also influences to a marked degree the amount of shear applied to the material and the frictional heat generated thereby. The depth of the flight also affects the amount of heat generated by shear and the transfer of heat to the material by direct contact with the barrel.

The output of an extruder does not necessarily increase in direct proportion to the increase in screw speed or power input. An economical speed which gives maximum output per unit of power input therefore is used as the operating speed. This will of course, vary with different

materials and can be adjusted by temperature regulation and screw design.

b) Helix angle

One of the mysteries surrounding the extruder screw design is the apparent sanctity of the 'square' helix angle. The competing requirements are a steep angle to resist back pressure flow and a shallow angle to provide the least tortuous path for drag flow. The universally accepted normal helix angle is 17.66°.

c) Residence time

Residence time is the period of time the polymeric materials actually spend in the extruder.[25] It can be used to analyse the the mixing process, the chance of degradation and process design in an extruder.[26] Other factors being constant, the residence time in the screw is proportional to its effective length and inversely proportional to speed or output. Thus factors dependent on residence time such as melting, heat transfer, heating between melting and final temperatures, distributive mixing and reduction of solid particles and temperature variations in the melt pumping section will be similarly influenced, and a longer screw will tend to offset limitations occurring with increased speed.

d) Other factors

Various other factors such as degree of mixing required, viscosity, transition temperature, nature and properties of the materials extruding, all influence the design of the screw. The effects of variations in screw characteristics may be summarised as follows:

1. Deeper channel: Conveys more material but takes longer to complete melting.
2. Fast running: Maximizes output but solids persist further along the screw.
3. Shallower channel: It can help fast running to increase output because of more efficient melting but the danger is that the resultant high shear might lead to overheating.

1.2 PRINCIPLES OF SINGLE SCREW EXTRUSION

1.2.1 General

The earliest attempts to formulate a mathematical theory of screw pumps are due to Finlayson and Rowel.[27] They published expressions for the output, the power requirements, and the efficiency of single screw machines. Their work was based on the general theory of lubrication developed by Reynolds[28] and Navier.[29]

1.2.2 Functional zones in an extruder

a) Feed zone

The function of the feed zone is to preheat the polymer and convey it to the subsequent zones. The screw depth is constant and the length of this zone is such as to ensure a correct rate of feed. Feed materials, however, differ widely in their physical form and it has been found by experiment that the helix angle most suitable for one form of material is not necessarily the best for another. Also the coefficient of friction varies considerably according to the form of the feed material as well as its nature.

As it is assumed that the metering zone of the screw controls the output it is important that the feed zone should be capable of conveying sufficient material to keep the metering zone full. The performance of the feed zone of the screw has a marked influence on the output of the machine but the influence of the helix angle in other zones of the screw has a smaller effect.[30] On the other hand it is equally important to ensure that the supply of material from the feed zone is not too great to overrun the metering zone. A pronounced departure from this balance either way will result in surging or pulsation[31] so that it is necessary to exercise reasonable care in the selection of a compression ratio to suit the bulk factor of the feed material. Compression ratio[32-33] is the ratio of the volume of one screw flight in the feed zone to the volume of a flight in the metering zone.

b) Compression zone

Compression zone or transition zone has decreasing channel depth for achieving compression ratio. This zone must be designed not only to compact the material by removing the occluded air but also to improve its thermal conductivity. Moreover, this zone conforms to the rate of melting and change of volume as the material pass from the solid to the viscous state. Furthermore, during its passage through the compression zone the material should become sufficiently viscous and deformable to be able to absorb energy from shear so that it may be heated and mixed uniformly throughout its mass.[34-35]

c) Metering zone

The metering zone is the final part of the screw and acts rather as a metering pump from which the homogenized polymeric material is delivered to the die system at constant volume and pressure.[36-38] This zone is associated with constant screw depth. The mechanisms of drag flow, pressure flow, and leakage flow may be envisaged as operating in the metering zone and the interaction of the variables of this part of the screw and die system was extensively studied.[39-44] The desirable depth of metering zone on a screw is closely related to the mean viscosity of the material passing through the section.

1.2.3 Flow mechanism

a) Conveying

Solids conveying may limit the output of an extruder. In solid conveying action at least three process are involved.[45-49]

1. Flow in the hopper or feed pipe
2. Filling of the screw channel from the feed throat
3. Conveying by the screw from the open feed section into the closed barrel and compaction in the latter.

When the material sticks to the screw only and slips on the barrel the screw and the material would simply rotate as a solid cylinder and there would be no transport. When the material resists rotation in the barrel and slips on the screw, it will tend to be transported axially, like a normal, deep channelled, solid conveying Archimedian screw.

b) Melting

Analysis of polymer behaviour during melting was based on screw push-out experiments.[50-58] As the polymer is conveyed along the screw, a thin film softens and melts at the barrel wall. This is usually by means of conducted heat from the barrel heaters, but could be frictional. The screw scrapes off the melted film as it rotates. The molten polymer moves down the front face of the flight to the core and then sweeps up again to establish a rotary motion in front of the leading edge of the flight. Other

solid granules or parts of the compacted slug of polymer are swept into the forming 'melt pool'. The process is progressive until all the polymer is melted.

1.2.4 Analysis of flow

a) Drag flow

In practice, there is friction with both screw and barrel, and this leads to the principal transport mechanism, drag flow. This is literally the dragging along by the screw of the melt as a result of the frictional forces. The drag flow is equivalent to the viscous drag between stationary and moving plates separated by a viscous medium. It constitutes the output component for the extruder.

$$\text{Drag flow} \quad Q_d = \frac{1}{2}\,\pi^2\, D^2 NH\, \sin\phi\, \cos\phi^{59} \ldots\ldots (1.1)$$

where D is the screw diameter

N, the screw speed

H, the channel depth, and

ϕ, the Helix angle.

b) Pressure flow

Pressure flow is caused by the pressure gradient along the screw. There is high gradient along the screw. There is high pressure at the output end, low, at the feed end and this pressure gradient opposes the

drag flow.[30] It is important to note that there is no actual flow resulting from the pressure, only an opposition.

$$\text{Pressure flow } Q_p = \frac{\pi D H^3 \sin^2\phi}{12\eta} \frac{dP}{dL} \quad \ldots(1.2)$$

where D is the screw diameter

H, the channel depth

ϕ, the helix angle

η, the fluid viscosity, and

$\frac{dP}{dL}$, the pressure gradient.

c) Leakage flow

The final component in the flow pattern is leak flow or leakage flow. It is the flow into the finite space between screw and barrel, through which material can leak backwards. This is also a pressure-driven flow and of course it opposes the drag flow.

$$\text{Leakage flow } Q_l = \frac{\pi^2 D^2 E \delta^3 \tan\phi \Delta P}{12\eta e L} \quad \ldots(1.3)$$

where

D is the screw diameter

E the factor for eccentricity of the screw

δ the clearance space

ϕ the helix angle

ΔP the overall pressure drop along the screw

η the fluid viscosity

e the flight width, and

L the effective screw length

The theoretical calculation of leakage flow for both pressure and drag flow effects has also been developed by Mohr, Mallouk and Booy,[61] who considered the flow across the flight lands in a direction at right angles to the axis of the screw.

1.2.5 Total flow and output

If the material is incompressible, the total output of the extruder is given by the sum of the drag flow Q_d, the pressure flow Q_p and the leakage flow Q_l[62]

Total output of the extruder ie., $Q = Q_d - Q_p - Q_l$ (1.4)

since both Q_p and Q_l will have opposite signs to Q_d

However leakage flow is very small compared with drag flow and pressure flow and may be neglected in finding the total flow. So the output Q is obtained by summing the expressions for drag flow and pressure flow.

$$\text{ie., } Q = Q_d + Q_p = \tfrac{1}{2}\,\pi^2 D^2 NH \sin\phi\cos\phi - \frac{\pi DH^3 \sin^2\phi\ P}{12\eta L} \qquad (1.5)$$

For a given extruder L, D, H and ϕ are all fixed. Thus on simplification,

$$Q = \alpha N - (\beta P/\eta) \qquad (1.6)$$

So the practical variables influencing the output of the extruder are:

the screw speed N

the head pressure P

the melt viscosity η.

1.2.6 Heat and power requirement

One of the main functions of an extruder is to raise the temperature of the feed material usually from ambient to a temperature at which it can flow and suitably form to a desired shape. It is therefore, necessary to supply heat energy to the material at a rate which will produce the temperature required for this operation. In addition to the energy necessary to heat the material, power must be supplied to the screw in order to turn it against the frictional and viscous resistance of the material in the screw flights. It will be readily appreciated that these two energy mechanisms are closely interrelated since an alteration in the rate of supply of one will produce a change in the other. Conventional melt flow theories are available for determination of screw power for normal extrusion operations[63-64] and the total screw power requirements

can be [illegible] by the methodes given by Mohr et al.[65] and Gore and McKelvey.[64] Conventional melt flow theories are available for determination of screw power for normal extrusion operations.[65,66]

1.2.7 Mixing

In addition to temperature, flow rate and pressure, the uniformity of composition of the polymer being extruded (for knowing the condition of the polymer leaving the extruder barrel) is an important criterion for the evaluation of the performance of the screw. A uniform composition may be obtained by a proper laminar mixing of the polymer. Mixing consists of two processes viz., one is the dispersion of the particles of the material being processed (ie., dispersive mixing) and the other is their uniform distribution throughout their entire volume (i.e., distributive mixing) Non-uniform composition (insufficient mixing) leads inevitably to poor properties, and poor external appearance of the product as well as to non-uniform distribution of its properties.

Dispersive mixing during the extrusion process consists of overcoming the cohesion of particles of the material and takes place due to shear stress in the surrounding fluid. On the other hand distributive mixing consists of changing the difference in composition of the material in various places and is affected by a relative motion of components.

1.2.8 The extrusion die

The function of an extrusion die is to size and shape the polymer melt delivered by the screw into a required cross section.[67] The die forming zone is essentially always a pressure consuming zone.[68-69] The pressure required to force the melt through the die is called die head pressure.[70] The variables that affect the die head pressure and hence the key factors in the practical die design are:

1. The geometry of the flow channel in the die
2. The rheological properties of the polymer melt[71,72]
3. The temperature distribution in the polymer melt
4. The flow rate through the die
5. Product geometry

In addition to the die land/orifice thickness ratio, the surface finish, the compound lubrication, the filler loading, the construction of the die upstream of the land and the system of product sizing to be used are to be mentioned for the proper die design. Generally, the size (cross sectional area) of the extrudate is determined by controlling the screw speed relative to the line speed. Besides limited shape control is possible by adjusting certain operating conditions.[73-74]

The simulations of flow in dies are based on the non-slip boundary condition for velocity at the solid walls.[75-77] The breaker plate/screen pack

before the die ensures pressure in the screw of the extruder, thus enabling the material to be worked and sheared and to be properly homogenized. Moreover, the breaker plate requires special attention not only as to its design and construction but also to ensure a proper streamlined relationship with the other parts of the equipment with which it is in contact.

There are three systems of extrusion dies known as straight-through, crosshead, and offset respectively, depending on the direction of the resulting extrusion and take-off relative to the direction of melt feed from the extruder.

Straight–through dies are obviously those dies whose axes are arranged to be in line with the direction of supply of melt. This type of dies are commonly used for the extrusion of pipe, rod, profiles, sheet and by means of a curved feed conduit, of tubular and flat film. Crosshead dies are arranged with their axes at an angle to their feed supply usually 90^{0} but 45^{0} and 30^{0} are also used. This type of dies are used for the production of insulated wires, cables and filaments. Offset dies have been developed from crossheads to combine the advantages of this form of side–feed die assembly with those of the straight–through type. Offset dies are popular for the production of pipe where the lack of a spider and also the ease of applying temperature control to the mandrel do much to improve the quality of the product.

In another way, extrusion dies can be broadly classified as:

1. Large aspect-ratio (width to thickness) dies[78] which give a uniform thin planar or annular extrudate.
2. Profile dies[79-80] which have aspect-ratio of the order of 1 to 10).

1.2.9 The extruder or screw characteristics

The product of extrusion is realized by forcing the melt through a shaping die to give a profiled, continuous extrudate.[81]

1. If there were to be no pressure build-up for example, no breaker plate or die, the output would be at its maximum, Q_{max}, we can use the drag flow ideal equation.

$$Q = Q_{max} = \frac{1}{2} \pi^2 D^2 N H \sin\phi \cos\phi$$

2. If there is maximum resistance and $Q = 0$, and we can equate the drag flow and pressure flow expressions.

i.e., $$\frac{1}{2} \pi^2 D^2 N H \sin\phi \cos\phi = \frac{\pi D H^3 \sin^2\phi \; P_{max}}{12 \eta L}$$

i.e., $$P_{max} = \frac{6 \pi D L N \eta}{H^2 \tan\phi} \quad \ldots\ldots(1.7)$$

These points represent the extremes in the Fig.1.3 of the extruder or screw characteristic.[37]

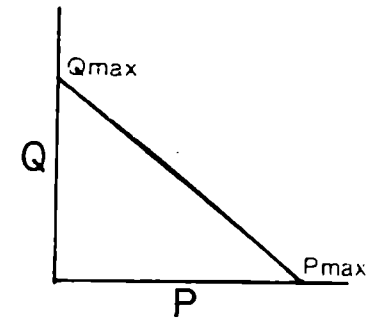

Fig.1.3 The extruder or screw characteristic

1.2.10 Interaction of screw and die characteristics

A die at the extruder outlet, requires head pressure[82,83] to function i.e., the pressure is needed simply to force the melt through the die. The die characteristic is thus opposite in form of screw characteristic as in the Fig. 1.4.

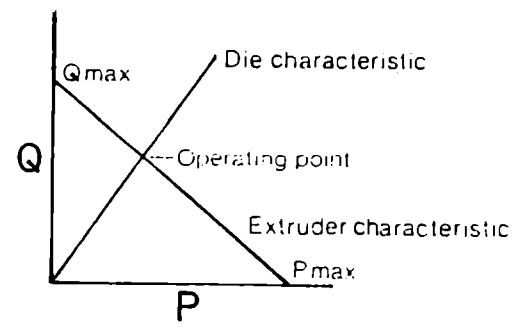

Fig.1.4: Interaction of screw and die characteristics

The maximum output will result from maximum pressure. The intersection point is the operating point, where the [illegible] operating

conditions are obtained. The output 'Q' of individual die depends, obviously on their shapes. In general,

$$Q = KP \tag{1.8}$$

where K is the shape dependent factor.

1.2.11 Variation in extruder and die characteristics

The position of the lines in the above figure will be changed by changes in operating conditions. If 'N', the extruder speed, is increased, the extruder characteristic moves up. If the die dimensions are changed e.g., the radius 'R' of the cylinder is increased, the slope of the die characteristic is increased. A family of parallel screw or extruder characteristics can be drawn for various screw speeds, N as shown in the Fig. 1.5.

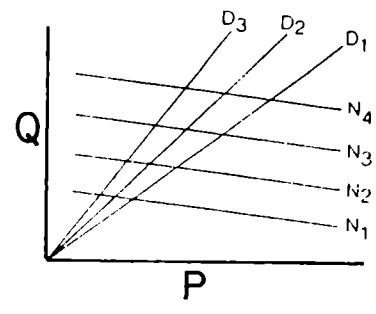

Fig.1.5 Family of screw characteristics with various die intersections

1.3 THE MULTI-SCREW EXTRUDER

a) The twin screw extruder

A twin screw extruder is a machine with two Archmedian screws. It acts as positive displacement pumps with little dependence on friction, and this is the main reason for their choice for heat sensitive materials.[84] There is a variety of twin screw extruders with vast differences in design, principle of operation and field of application.[85-87] Counter rotating machines, if conjugated may have no passage at all for material to move around the screws, it must move axially towards the die end. Likewise co-rotating machines will have no passage around each screw and only a small and tortuous one round both, also leading to positive axial flow. Thus L/D ratio is unimportant for propulsion and so there is no long metering zone.

The length must of course, be sufficient for proper melting of the polymer. Also because of the positive pumping action, the rate of feed is not critical in maintaining output pressure. The conveying is not by drag flow, and this allows good control of shear rate and hence temperature. A comparative study between single screw and twin screw extruders is given in the Table 1.1.[88]

Table 1.1: Points of comparison of extruders

	Single screw	Twin screw
1. Flow type	Drag	Near positive
2. Residence time and distribution	Medium/wide	Low/narrow (useful for reaction)
3. Effect of back pressure on output	Reduces output	Slight effect on output
4. Shear in channel	High (useful for stable polymers)	Low (useful for PVC)
5. Overall mixing	Poor/medium	Good (useful for compounding)
6. Power absorption and heat generation	High (may be adiabatic)	Low (mainly conductive heating)
7. Maximum screw speed	High (output limited by melting, stability etc.)	Medium (limits output)
8. Thrust capacity	High	Low (limits pressure)
9. Mechanical construction	Robust, simple	Complicated
10. First cost	Moderate	High

1.4 RUBBER EXTRUSION

Eventhough the process of rubber extrusion has been known for more than a century, only limited number of literature is available on this subject compared to the literature on the thermoplastic extrusion. Some of the handbooks[89-92] and literature[93,94] on rubber discuss rubber extrusion. The first rubber extruders were built for hot feed extrusion. These machines are fed with warm material from a mill or other mixing device. Around 1950, machines were developed for cold feed extrusion. The advantages of cold feed extruders are found to be

1. Less capital equipment cost
2. Better control of stock temperature
3. Reduced labour cost
4. Capable of handling a wider variety of compounds.

For rubber processing in a single screw extruder, the screw rotates in a tightly fitted barrel, thereby transmitting mechanical energy into the rubber compound. As the temperature of the rubber increases, the plasticity is lowered to such a level that the rubber can be shaped by passing through a die located at the end of the barrel. To achieve turbulence in the rubber, it is necessary for the rubber to grip the metal surfaces, enabling shear to take place.[95] If the rubber slides on the steel surface, more frictional heat is generated for heat transfer.

The extrusion process affects the output rate, extrudate temperature, Mooney viscosity and scorch time of the compound.[96] Maximum output is limited by the maximum permissible heat history of the compound (Scorch time)[97]. At low screw speeds, output rate is nearly directly proportional to screw speed (rpm) for most compounds. As the screw speed increases toward the high end, the output rate decreases.

1.4.1 Features of rubber extrusion

1. A feed opening, placed tangentially to the screw and equipped with a driven feed roll to facilitate the feeding of strips.
2. A screw and barrel just long enough to compact the material and force it through the breaker plate (if any) and the die.
3. The barrel to be heated to a relatively low temperature—usually by steam in order to conserve heat in the material.
4. A water–cooled feed section and screw, to prevent sticking and pre-curing of the stock respectively
5. The feed screw to be deeply cut in order to accept a large volume of material, and designed with often constant depth and decreasing pitch to give a compression ratio without unduly increasing the amount of shear.
6. The screw is to be driven at a relatively low rotational speed in order to avoid excessive frictional heat.

7. As a result of the above points, the machine need not be particularly robust in its construction and thrust bearing arrangements, and the drive motor can be relatively small.

1.5 THERMOPLASTIC EXTRUSION AND ITS FEATURES

In this process of extrusion, the thermoplastic material is propelled continuously along a screw through regions of high temperature and pressure, where it is melted, compacted and finally forced through a die, shaped to give the final profile.

Features

1. A feed opening suitable for handling of cold material in granulated, chip, cube, or powder form, surmounted by a feed hopper.
2. A longer screw (usually having a constant pitch and decreasing depth) and barrel in proportion to their diameter i.e., a greater L/D ratio. The barrel to be lined with or made from a corrosion—resistant alloy. Depending on the particular screw design, it will also give a considerable heat due to frictional work and develop a pressure gradient along its length.
3. A breaker plate and screen pack and/or other restrictive system to be fitted.
4. A screw designed to provide compression, mixing, and shear of the feed material.

5. The barrel to be heated to a high temperature in a number of zones, to give a heat gradient and the temperature to be accurately controlled. Provision for controlled cooling of the barrel, to remove excess frictional heat, must also be considered.
6. A water-cooled feed opening.
7. Provision for water cooling or heating of the screw.
8. The feed screw to be easily interchangeable so that screws of the different designs, both deeply and shallow cut and with different compression ratios, can be used as required by the various polymers.
9. Provision for driving the feed screw at a wide range of speeds and for varying this speed without stopping the machine.
10. In order to stand up to the very high pressures which are often encountered in thermoplastics extrusion, machines for this purpose must be robust, capable of withstanding very high thrust loadings, and equipped with drive motors of ample power.

1.6 MODES OF FEEDING IN EXTRUSION

Feeding of a polymer to a single screw extruder can be done by adopting any of the following methods.

1. Starve feeding through the use of metering device.[98]
2. Flood feeding (normal feeding) through a hopper.[99]
3. Force feeding or power feeding by using hopper compactor.[100]

Among the above three approaches, starve feeding is commonly employed for improving the operating versatility of single screw extruders.[101] For example, the same screw can handle a wide range of materials and performance requirements often better utilizing horse power availability.[102]

1.6.1 Flood feeding, force feeding and starve feeding

The vast majority of single screw extruders are gravity fed directly from hoppers or fed on a driven feed roll, mounted above the feed section. With this arrangement, known as flood feeding, the channels in the feed section run full and the output of the machine is determined by the capacity of the extruder to process and pump the polymer.[99,103] That is flood feeding is a mode of feeding in extrusion in which the screw will be given the polymer material as much as it can normally take.

In some cases, the feed stock is forced into the extruder using a crammer, this has a particular application in some powder processes where pressure generation capacity is poor. So force feeding is a type of feeding in which the screw will be forced.to take more material than it can normally take by an external power or force. Occasionally extruders are trickle fed to overcome feed problems at the entrance to the extruder and to avoid hopper bridging. A similar scheme, but with rather different objectives, is the metered starve feeding of extruders. In this arrangement, the extruder is fed at a controlled rate below the flood fed

rate in order to improve certain performance characteristics.[98,102-106] The principle of starve feeding is effectively utilized in the vented screw extruders. To permit vapour release, the screw channel at the vent should be partially filled.

1.6.2 Pumping and starvation phenomena of thermoplastics

When exit pressure of an extruder is lowered, the output of an extruder immediately increases. If, however, the material fed to the extruder is metered and kept below the level corresponding to the specific output pressure, the extruder is starve-fed.[107] In this case, the output cannot increase to satisfy the lower end-pressure requirement and must remain at the level at which the melt is being supplied to the extruder.

At first this seems to violate the relationship between output and extruder head pressure, which is defined by screw geometry, operating conditions, and physical properties of the melt. The extruder therefore, takes internal evasive action, by filling the first portion of the screw channel only partially, causing the pressure to rise only further down channel. The semifilled channel of the polymer results in a decrease in the drag flow term, which is normally computed under the assumption of a completely filled channel.

The first reported work on metered starve feeding was by Russel J.Nichols and George A.Kruder in 1974.[102] These workers ran an 89 mm

diameter extruder at rates of 50% and 75% of their flood fed capacity and found that improvements in die pressure variation (and hence dimensional consistency and a reduction in the specific power consumption i.e. the energy required to process unit mass of polymer) could be expected. They also suggested that starve feeding may be a suitable technique for running extruders under conditions for which the screw was not specifically designed. In this way, starving can be seen as a tuning device to improve the performance of non-optimum screws.

In 1978, McKelvey and Steingiser[98] reported much more significant advantages resulting from their trials on a 230 mm diameter extruder when run under starved conditions. Substantial reductions in pressure fluctuations were found and specific power consumption savings of 50% were measured. These authors limited the degree of starvation of the machine so that minimum throughput was about 80% of flood fed capacity. The large drop in screw torque requirements offered attractive advantage and there was some response by extruder manufactures particularly in the United States where a few machines are now equipped with starve feeders.

The melting mechanism associated with starve feeding was studied by Isherwood et al.[103,108] who carried out trials on a 38 mm diameter laboratory extruder fitted with screw extraction facilities. Three polymers were processed. One of which was in both granular and powdered form.

It was found that melt initiation was later, but once initiated, melting took place more rapidly in starve fed situations compared with the flood fed case. Isherwood and his co-workers related the observed melting patterns to the measured pressure fluctuations and specific power consumptions, explaining the behaviour in terms of greater solid mobility due to the closer packing associated with starving. The improvements in performance were modest, however, and were only apparent at starving levels of up to 10% (i.e, throughput is 90% of flood fed rate). For lower throughputs performance deteriorated. Moreover, for larger machines the effects of starve feeding are more attractive with a view to commercial application. Under starved conditions a compromise between the saving in power per unit output and the loss due to reduced production rate leads to the minimum economic extrusion rate.[109-113] The loss in production rate can be substantially compensated by running the starve fed machine at a higher speed.[103]

The pumping efficiency[114], the fluctuation of pressure[103], screw torque[102], of a starve fed extruder had been reported. Since starve feeding is operating at constant pressure, the pressure flow and leakage flow can be minimised. So the output is only due to significantly by drag flow. Since shear stress is less but uniform in starve feeding, comparing to flood feeding and force feeding, the die flow instabilities such as melt fracture, shark skin etc. will be reduced.[102]

1.6.3 Pumping and starvation characteristics of rubber compounds

Experimental studies of screw pumping characteristics of rubber compounds were formulated by G.R.Vila.[115] He found that throughput (Q) increased linearly with screw speed, independent of the viscosity of the compound. The power consumption of the extruder was found to increase linearly with both screw speed and viscosity of the compound. He found that the temperature of the extruded material similarly increased with screw speed and viscosity.

W.Meskat and Pigott[116] in 1951 reported measurements on a 25 mm Bench extruder with a 3.17 mm screw channel depth and a pitch of 25.4 cm. The screw length from the part to the end of the screw was 190 mm. At open discharge, Pigott examined the screw and found it to be starved. The screw became filled with increasing die resistance. The extruder was fully filled and pressurised at Zero discharge. Under these conditions, Pigott reported the increase in pressure developed with screw speed. When the clearance between the outer diameter of the screw and the inner diameter of the barrel increased, the ability of the screw to develop pressure rapidly reduced. Pigott and E.S.Echen[117] published the screw characteristic curve.

In 1986-87, Brozoskowski, White, and their co-workers[118-120] at the Institute of Polymer Engineering, at the University of Akron

published a series of papers on the pumping and starvation characteristics of cold feed rubber compounds in screw extruders. These authors used a 37.5 mm 20 L/D NRM screw extruder, a 44.8 mm 10 L/D Monsanto screw extruder and a 32 mm 12 L/D Boy screw injection moulding machine operating as a screw extruder. The experiments were carried out with two rubber compounds, PTT, a typical passenger tyre tread compound, and TTT, a typical truck tyre compound Brzoskowski et al. found starvation to occur under most conditions in their investigations of screw extrusion. The screws were fully filled in the region near the feed section. In some cases, the starved region consisted of a continuous strip of rubber moving along the leading flight of the screw. In other cases, it consisted of chunks of rubber compound moving along the leading flight.

The character of the starved regions observed by Brozoskowski et al. was strongly dependent upon the feed section of the screw extruder. Introduction of power feed or force feed was found in one extruder to eliminate starvation. Increase of the width of the feed strip was found to reduce starvation. The break up of rubber compound into chunks as described in the previous paragraph, appeared to be due to the design of the feed section. Brozoskowski et al. found that synthetic rubber (SBR-BR) compounds moye readily tore into chunks than natural rubber compounds. This was attributed stress-induced crystallization which prevented the growth of tears in the natural rubber compound.[121] Such tearing occurs in the feed section.

The starvation levels of cold feed rubber extruders were treated quantitatively by Brozoskowski, White and their co–workers.[119-120,122] The length of the filled region of the extruder screw was found to depend primarily, and perhaps only on the head pressure. The length of fill of two of the screws studied as a function of head pressure. The filled length may be seen in each case to be a strong monotonic increasing function of pressure.

The screw characteristic curves for fully filled and starved machines have also been investigated by Brozoskowski, White and their co–workers.[119-120,122] The comparison of the screw pumping characteristics of the starved and fully filled 44.8 mm screw was discussed. For both starved and fully filled screw extruders, the output increases with screw speed N. It can be seen for the fully filled extruder (with operating power feed i.e. force feed) that the output decreases with increasing pressure development. For the starved extruder, the output appears independent of die pressure.

The outputs are independent of head pressure but increase with both screw speed and width of feed strip. Moreover, starvation in single-screw extruders has been studied by Shin and White[123] who found that the length of fill for the different rubber compounds not only increases with pressure but with the ratio of pressure to shear viscosity.

1.6.4 Extent of partial filling

Various situations of partial filling are shown diagramatically in Fig. 1.6. If the channel is filled to a very small extent as in the Fig.a,

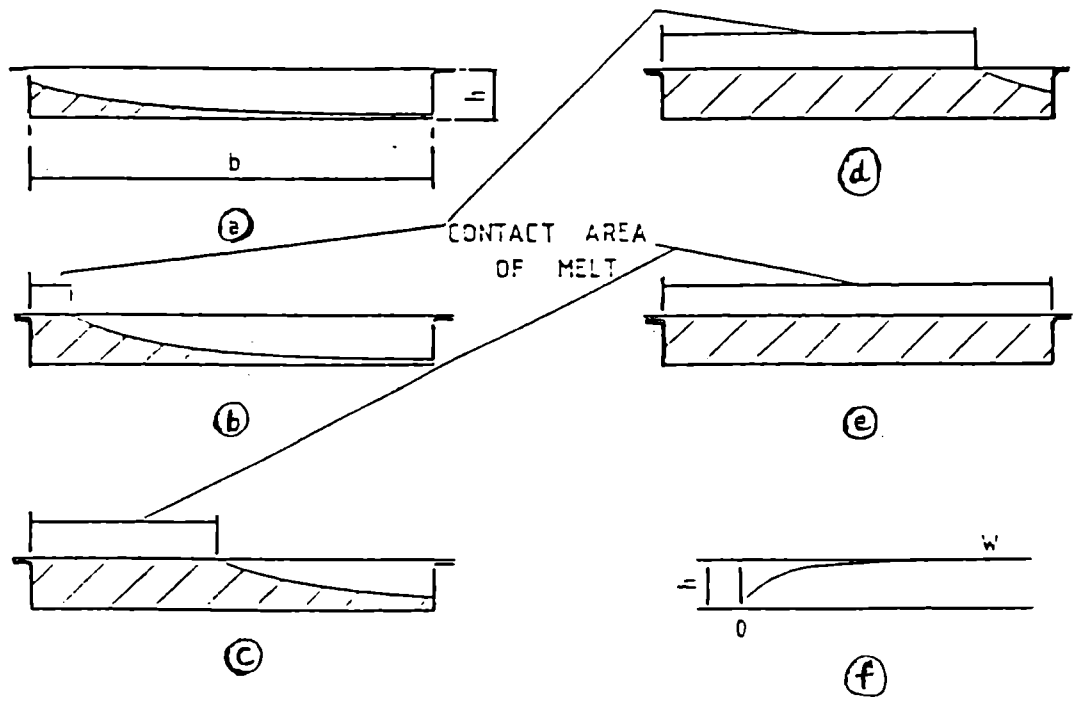

Fig. 1.6 Melt cross-section of partially filled channels

the melt will form a thin film over the screw surface and rotate without touching the barrel and thus without any forces tending to move it along

the screw. Any material which adheres to the barrel or is trapped in the flight clearance will tend to be collected on the leading face of the screw flight (Fig.b) by the transverse movement. The material represented by the shaded area will be subjected to a shear force at the barrel, opposed by an equilibrium force on the much larger surface in contact with the screw, the shear stress and hence shear rate at the barrel will thus be much higher than at the screw, resulting in a velocity gradient as in Fig.f. As the degree of filling increases through the situation represented by Fig.c, the area in contact with the barrel will increase faster than both the volume of the melt, represented by the shaded area and the area in contact with screw, so that shear stress and shear rates tend to become nearly equal and hence the pumping efficiency increases.[53-88] When the channel is partially filled as in Fig.d, (i.e. about 90% filled) the shear conditions and pumping efficiency will be more uniform than that in a completely filled, or thickly populated screw channel[108] as in Fig.e.

Since the shear is more uniform in the partially filled channel this results in more uniform heat transfer and temperature distribution among the thin layers of polymers. So thermal homogeneity is easily achieved. In a completely filled channel (as a result of flood feeding and force feeding) since non-uniform shear operate and hence non-uniform heat transfer and temperature distributions occur along with thick insulating layers of polymer and so the thermal homogeneity may not effectively attained.

1.7 SCOPE AND OBJECTIVES OF THE PRESENT INVESTIGATION

Starve feeding of single screw extruder was described as an important means of improving the performance characteristics of the extruder. In addition to such improvement with versatility, the starve feeding technique also may affect the mechanical properties of the extrudate since the heat transfer and mixing characteristics in the starve fed and flood fed extruders are not the same. Since the material is more loosely packed in the channels of the starve fed extruder, there may be greater bed mobility and uniformity. Further, the thermal and shear induced degradation are also less since possibilities of developing local high temperatures are less compared to a densely compacted extruder bed. This study has been undertaken mainly to explore the effect of feeding rate on the mechanical properties of rubber and plastic extrudates since the effect of feeding rate has not been analysed from this angle so far.

In the present study, it is proposed to investigate in detail, effect of feeding rate on the mechanical properties of the following polymers:

1. A fairly heat sensitive and regionally important rubber: Natural rubber (NR).

2. A very widely used general purpose synthetic rubber: Styrene-butadiene rubber (SBR).
3. A thermally stable synthetic rubber: Isobutylene–isoprene rubber (IIR).
4. A semi crystalline standard plastic: Low density polyethylene (LDPE)
5. An amorphous standard plastic: polystyrene (PS)

The objectives of the proposed study are:

1. To determine the effect of feeding rate on the mechanical properties of LDPE & PS, and gum and filled compounds of NR, SBR, & IIR.
2. To find out the optimum feeding rate at which maximum mechanical properties are obtained in the case of these polymers.
3. To evaluate the effect of temperature and revolutions per minute (rpm) on the mechanical properties of NR, SBR, IIR, LDPE and PS with feeding rate.
4. To make a systematic study on the structural changes in the polymers resulting from the changes in the feeding rate.

This thesis is divided into the following chapters:

Chapter 1	Introduction
Chapter 2	Experimental techniques
Chapter 3	Effect of feeding rate on the technical properties of gum, NR, SBR and IIR vulcanizates
Chapter 4	Starved extrusion for the improvement of mechanical properties of filled NR, SBR and IIR vulcanizates
Chapter 5	Effect of feeding rate on the mechanical properties of LDPE and PS
Chapter 6	Summary and conclusions

REFERENCES

1. R.W.Wilson, D.Chan and C.James Lee, Polymer Eng. Sci., 26(2), 144 (1986).

2. G.Schenkel, Intl. Polym. Process, 3, 3 (1988).

3. R.E.Colwell and K.R.Nickolls, Ind. Eng. Chem., 51, 841 (1959).

4. R.M.Griffith, Ind. Eng. Chem. Fundamental. 1, 180 (1962).

5. R.T.Fenner, Polymer, 16, 298 (1975).

6. H.Kunhle, J. Polym. Eng., 6, 51 (1986).

7. M.L.Hami and J.F.T.Pitman, Polym. Eng. Sci., 20, 339 (1980).

8. D.Roylance, Polym. Eng. Sci., 20, 1029 (1980).

9. H.Kuhnle, Kunststoffe, 72, 267 (1982).

10. M.Viriyayuthakorn and B.Kassahun, SPE Tech. Papers, 30, 81 (1984).

11. K.P.Choo, M.L.Hami and J.F.T.Pitman, Polym. Eng. Sci., 21, 100 (1981).

12. R.Brozoskowski, J.L.White, W.Szydlowski, N.Nakajima and K.Min, Int. Polym. Process, 3, 134 (1988).

13. E.E.Agur and J.Vlachopoulos, Polym. Eng. Sci., 22, 104 (1982).

14. J.F.T.Pittman and K.P.Raschid, J.Polym. Eng., 5, 1 (1985).

15. H.E.H.Meijer and C.P.J.M.Verbraak, Polym. Eng. Sci., 28, 758 (1988).

16. H.R.Simonds, A.J.Weith and W.Schack, "Extrusion of Rubber Plastics and Metals", Van Nostrand Reinhold, New York (1952).

17. Chris Rauwendaal, "Polymer Extrusion", Hanser Publishers, Munich (1986).

18. A.L.Griff, Ed., "Plastics Extrusion Technology", Van Nostrahd Reinhold, New York (1968).

19. P.N.Richardson, "Introduction to Extrusion", Society of Plastics Engineers, Inc. (1974).

20. J.A.Brydson and D.G.Peacock, "Principles of Plastics Extrusion", Applied Science Publishers Ltd., London (1973).

21. J.R.A.Pearson, "Mechanics of Polymer Processing", Elsevier, London (1986).

22. S.Middleman, "Fundamentals of Polymer Processing", McGraw-Hill, New York (1977).

23. J.F.Cookson and F.Tunnichiff, Trans. Plast. Inst., 19, 38 (1951).

24. J.R.A.Pearson, Int. J. Heat Mass Transfer, 19, 405 (1976).

25. R.A.Weiss and H.Stamato, Polym. Eng. Sci., 29(2), 134 (1989).

26. C.J.Rauwendaal, Polym. Eng. Sci., 21, 1092 (1981).

27. D.Finalayson and H.S.Rowel, Engineering, 114, 606 (1922); 126, 249 (1928).

28. O.Reynolds, Phil. Trans. R.Soc., 177, 157 (1986).

29. C.L.M.H.Navier, Mem. Acad., Sci. Inst. Fr., 6 (1822).

30. L.B.Ryder, SPE J. 17, 731 (1961).

31. R.Kirby, SPE Tech. Pap. 10, 8 (1962).

32. P.H.Squires, J.B.Paton, W.H.Darnell, F.M.Cash, J.F.Carley, "Processing of Thermoplastics", E.C.Bernhardt (Ed.), Reinhold, New York for the society of Plastics Engineers (1959).

33. Y.Mori, N.Otatake and H.Igarashi, Chem. Engg., Tokyo, 18, 22 (1954).

34. L.F.Street, Int. Plast. Engg., 1, 289 (1961).

35. E.Beck.Kuststoffe, 52, 213 (1962).

36. H.O.Schiedrum and H.Dominighaus, Plastics Lond., 26, 81 (1961).

37. B.H.Maddock, SPE J1, 23, 23 (1967).

38. R.Pfluger, Kunststoffe, 52, 273 (1963).

39. E.M.Mount, J.G.Watson and C.I.Chung, Polym. Eng. Sci., 22, 779 737 (1982).

40. Y.Mori and T.K.Matsumoto, Rheol. Acta, 1, 240 (1958).

41. D.J.Weeks and W.J.Allen, J. Mech. Eng. Sci., 4, 380 (1962).

42. B.S.Clyde and W.A.Holmes—Wlaker, Int. Plast. Engg., 2, 338 (1962).

43. F.W.Kroesser and S.Middleman, Polym. Eng. Sci., 5, 231 (1965).

44. R.W.Flumerfelt, M.W.Pierick, S.L.Cooper. and R.B.Bird, Ind. Eng. Chem., 8, 354 (1969).

45. W.H.Darnell and E.A.J. Mol, SPE J., 12, 20 April (1956).

46. E.Broyer and Z.Tadmor, Polym. Eng. Sci., 12, 12 (1972).

47. Z.Tadmor and E.Broyer, Polym. Eng. Sci., 12, 378 (1972).

48. J.G.A.Lovegrove and J.G.Williams, J.Mech. Eng. Sci., 14, 114 (1973).

49. R.T.Fenner, "Principles of Polymer Processing", Macmillan, London (1979).

50. B.H.Maddock, SPE J, 15, 383 (1959).

51. L.F.Street, Int. Plast. Eng., 1, 289 (1961).

52. Z.Tadmor, I.J.Duvdevani and I.Klien, Polym. Eng. Sci., 7, 198 (1967).

53. I.Klein and Z.Tadmor, Polym. Eng. Sci., 9, 11 (1969).

54. J.Shapiro, A.L.Halmos and J.R.A.Pearson, Polymer, 17, 905 (1976).

55. A.L.Halmos, J.R.A.Pearson, Trottnow, Polymer, 19, 1199 (1978).

56. J.T.Lindt, Polym. Eng. Sci., 16, 284 (1976).

57. B.Elbirli, J.T.Lindt, S.R.Gottgetreu and S.M.Baba, Polym. Eng. Sci., 24, 988 (1984).

58. J.Dekker, Kunststoffe, 66, 130 (1976).

59. E.G.Fisher, "Extrusion of Plastics", (3rd Ed.), Newnes—Butterworth, London, p.47 (1976).

60. P.H.Squires, SPE J., 14, 24 (1958).

61. W.D.Mohr, R.S.Mallouk and M.L.Booy, "Processing of Thermoplastic Materials", E.C.Behshardt (Ed.), Reinhold, New York (1959).

62. W.L.Gore et al. Ind. Engg. Chem., 45, 969 (1953).

63. A.Berlis, E.Broyer, C.Mund and Z.Tadmor, Plastics and Polymers, June 1973.

64. R.J.Nichols, G.A.Kruder, SPE ANTEC 20, 14 (1974).

65. W.D.Mohr, R.S.Mallock and M.L.Booy, Int. Plast. Engg., 2, 54 (1962).

66. W.L.Gore and J.M.McKelvey, SPE J. 10, 20 (1954).

67. Z.Tadmor and C.G.Goyos "Principles of Polymer Processing", Wiley, New York (1979).

68. W.Michaei, "Extrusion Dies", Hanser Publishers, Munich (1984).

69. N.S.Rao, "Designing Machines and Dies for Polymer Processing with Computer Programmes", Hanser Publishers, Munich (1981).

70. E.B.Bagley, J. Appl. Phys., 28, 624 (1957).

71. M.Mooney, J. Colloid, Sci., 2, 69 (1947).

72. M.Mooney and S.A.Black, J. Colloid Sci., 7, 204 (1952).

73. J.F.Stevenson, Rubb. Chem. Technol., 59, 651 (1986).

74. J.F.Stevenson, L.J.Lee and R.M.Griffith, Polym. Eng. Sci., 26, 233 (1986).

75. H.C.Lan and W.R.Schowalter, J. Rheol., 30, 193 (1986).

76. E.Uhland, Rheol. Acta, 15, 30 (1976).

77. A.I.Isayev, N.Famili, J. Plast. Film Sheeting, 2, 269 (1986).

78. F.Rothemeyer, Kunststoffe, 59, 333 (1969).

79. T.J.Liu, Ind. Eng. Chem. Fundam., 22, 183 (1983).

80. G.P.Lahli, SPE J. (July), 19, 619 (1963).

81. W.Ast. Kunststoffe, 66, 186 (1976).

82. K.Ito, Japan Plastics, 4, 27 (1970).

83. M.B.Chejfec, Plast. Massy, 12, 31 (1973).

84. K.Eise, S.Jakopin, H.Herrmann, U.Burkhardt and H.Werner, Adv. Plast. Techn., 18, 39 (1981).

85. J.C.Maheshri and C.E.Wyman, Ind. Eng. Chem. Fundam., 18, 226 (1979).

86. Z.Doboczky, Plastverarbeiter, 16, 57 (1965).

87. W.A.Mack and R.Herber, Chem. Eng. Prog., 72, 64 (1976).

88. M.J.Stevens, "Extruder Principles and Operation", Elsevier, London Chap.4 (1985).

89. J.Lebras, "Rubber Fundamentals of its Science and Technology", Chemical Publ. Co. New York (1957).

90. W.J.S.Naunton, "The Applied Science of Rubber", Edward Arnold Ltd., London (1961).

91. C.M.Blow, "Rubber Technology and Manufacture", Butterworth and Co. Ltd., London (1971).

92. F.R.Eirich, Ed., "Science and Technology of Rubber", Academic Press, New York (1978).

93. E.G.Harms, Eur. Rubber Journal, 6, 23 (1978).

94. G.Menges and E.G.Harms, Kautschuk & Gummi Kunststoffe 25, 10, 469 (1972).

95. S.C.Stillwagon, India Rubber World 101, 50 (1939).

96. D.H.Smith and R.L.Christy, Rubber Chem. Technol., 45, 1434 (1992).

97. J.L.White, Int. Polym. Process, 7, 110 (1992).

98. J.M.Mckelvey and S.Steingisten, Plast. Eng., 751, June 1978.

99. B.Franszkoch and G.Menges, Plast. Eng., 10, 51 July, 1978.

100. J.G.A.Lovegrove, Plast. and Rubb. Process, 12, 125 (1979).

101. B.H.Maddock, SPE—15th ANTEC, 5, 211 (1959).

102. Russel J.Nichols, George A.Kruder, SPE J. 20, 462 (1974).

103. D.P.Isherwood, R.N.Pieris and D.Valamonte, Plast. Rubb. Process, Appl 4(3), 257 (1984).

104. J.M.McKelvey, Plast. Eng., 7, 45-49, (June, 1978).

105. L.Lopez-Latorre and J.M.McKelvey, Adv. Polym. Technol., 3(4), 355–364 (1983).

106. Dilhan M.Kalyon, "Applications of Continuous Mixers", Nicholas P.Cheremisinoff, (Ed.), Marcel Dekker Inc., New York, Chap.3 (1989).

107. Imrich Klein and Jules W.Lindau, "Introducltion to Polymer Science and Technology", H.S.Kaufman and Joseph J. Falcetta (Eds.), John Wiley and Sons, New York, Chap. 9 (1977).

108. D.P.Isherwood, R.N.Pieris, J.Kassatly and D.Valamonte, "Some Experiments on Metered Starve Feeding in the Extrusion Process", ASME Design and Production Engineering Conference, Washington, pp.135–144 (1982).

109. James M.Mckelvey, SPE ANTEC, Vol.24 (1978).

110. S.Middleman, Poly. Eng. Sci., 5(4), 230 (1965).

111. H.A.A.Helmy and J.Parnaby, Polym. Eng. & Sci., 16(6), 436 (1976).

112. C.Rauwendaal, SPE 43rd ANTEC Reprints (1985).

113. Harutun G.Karien, SPE 44th ANTEC (1986).

114. K.Ramamurthy and S.Lakshmanan Intern. Plast. Eng. & Technol., 1, 59 (1994).

115. G.R.Vila, Ind. Eng. Chem., 36, 1113 (1944).

116. W.Meskat and Pigott, Kunststoffe, 41, 417 (1951).

117. Pigott and S.Eccher, Trans. ASME, 73, 954 (1951).

118. R.Brozoskowski, J.L.White, F.C.Weissert, N.Nakajima, and K.Min. Rubb. Chem. Technol., 59, 634 (1986).

119. R.Brozoskowski, K.Kubota, K.Chung, J.L.White, F.C.Weissert, N.Nakajima, and K.Min., Int. Polym. Process, 1, 130 (1987).

120. R.Brzoskowski, and J.L.White, Int. Polym. Process, 2, 102 (1987).

121. H.W.Greensmith, L.Mullins and A.G.Thomas, "The Chemistry and Physics of Rubber like Substances", L.Bateman (Ed.), McLaren, London (1963).

122. K.Kubota, R.Brozoskowski, J.L.White, F.C.Weissert, N.Nakajima, and K.Min, Rubb. Chem. Technol., 60, 924 (1987).

123. K.C.Shin and J.L.White, Rubb. Chem. Technol., 66, 121 (1993).

CHAPTER 2

EXPERIMENTAL TECHNIQUES

EXPERIMENTAL TECHNIQUES

The materials used and the experimental procedures adopted in the present investigations are given in this chapter.

MATERIALS

2.1 POLYMERS

2.1.1 Natural rubber (NR)

ISNR-5 was supplied by the Rubber Research Institute of India, Kottayam, Kerala. The Indian standard specifications for this grade of rubber are given below.

Parameters	Limit
Dirt content, % by mass, max.	0.05
Volatile matter, % by mass, max.	1.00
Nitrogen, % by mass max.	0.70
Ash, % by mass, max.	0.60
Initial plasticity, (P_o), min.	30.00
Plasticity retention index, (PRI), min.	60.00

2.1.2 Styrene–butadiene rubber (SBR)

Styrene–butadiene rubber was synaprene 1502 grade supplied by Synthetics and Chemicals Ltd., Bareilly, U.P. It had a styrene content of 23.50 % by mass and Mooney viscosity [(ML (1+4) at 100°C)] of 52.

2.1.3 Isobutylene–isoprene rubber (Butyl rubber) (IIR)

Isobutylene–isoprene rubber was Exxon 065 with a Mooney viscosity, [ML(1+8) at 100°C] of 50;

2.1.4 Low density polyethylene (LDPE)

Indothene FS 300 was supplied by IPCL, Baroda; density (gm/cc) 0.922; melt flow index (gm/10 min), 6.

2.1.5 Polystyrene (PS)

General purpose grade (polystron–678, SFI); supplied by M/s.Polychem Ltd., Bombay.

2.2 OTHER INGREDIENTS

2.2.1 Zinc oxide (ZnO) (activator)

Zinc oxide was supplied by M/s.Meta Zinc Ltd., Bombay having the following specifications given below:

Specific gravity	5.570±0.08
Zinc oxide content	98%
Acidity	0.4% max.
Heat loss (2 hrs at 100°C)	0.5% max.

2.2.2 Stearic acid (co-activator)

Stearic acid was supplied by Godrej Soaps (P) Ltd., Bombay, and had the following specifications:

Melting point	50–69°C
Acid number	185–210
Iodine number	9.5 max.
Specific gravity	0.85±0.01
Ash content	0.1% max.

2.2.3 Dibenzthiazyl disulphide (MBTS) (accelerator)

Dibenzthiazyl disulphide was supplied by M/s.Bayer Chemicals, Bombay, having the following specifications:

Specific gravity	1.34
Melting point	165°C

2.2.4 Tetramethyl thiuram disulphide (TMTD) (accelerator)

Tetramethyl thiuram disulphide used in the study was supplied by M/s.Polyolefins Industries, Bombay, having the following specifications.

Melting point	136°C
Specific gravity	1.405±0.025
Ash content	0.5% max.
Moisture	1% max.

2.2.5 N–cyclohexyl–2–benzthiazyl sulphenamide (CBS) (accelerator)

N–cyclohexyl–2–benzthiazyl sulphenamide used in the study was pilcure. CBS was supplied by polyolefins Industries, Bombay, having the following specifications.

Ash content	0.5% max.
Moisture	0.5% max.
Specific gravity	1.25

2.2.6 Sulphur (crosslinking agent)

Sulphur was supplied by M/s.Standard Chemical Company Pvt. Ltd., Madras and had the following specifications:

Specific gravity	2.05
Acidity	0.01% max.
Ash content	0.01 % max.
Solubility in CS_2	98% max.

2.2.7 High abrasion furnace black (HAF N–330) (filler)

High abrasion furnace black was supplied by M/s.Carbon and Chemicals (India) Ltd., Kochi having the following specifications:

Idoine adsorption	80 mg/gm
DBP absorption	105 cc/100 gm
Mean particle dimension	32 nm

2.2.8 Aromatic oil (process oil)

Aromatic oil was supplied by M/s.Hindustan Petroleum Corporation Ltd. It had the following specifications:

Colour	Black coloured oil
Viscosity gravity constant (VGC)	0.98–1.0

2.2.9 Naphthenic oil (process oil)

It was supplied by M/s.Hindustan Petroleum Ltd., having the following specifications:

Colour	Light coloured oil
Viscosity gravity constant	0.85–0.9

2.2.10 Pilflex–13 (Antioxidant)

Commercial grade antioxidant pilflex–13[N–(1,3–Dimethyl butyl)–N'–phenyl–p–phenylene diamine] was obtained from Polyolefin Industries Ltd., Bombay.

2.2.11 Solvents

Benzene, toluene and p–xylene were of analytical grade.

2.3 EXPERIMENTAL PROCEDURE

2.3.1 Extrusion on a laboratory extruder

The basic extruder on which the feeding rate studies were done was a laboratory extruder attached to a Brabender plasticorder model PL 2000. Brabender plasticorder is a computerised torque rheometer system used for testing thermoplastics, thermosets and elastomers.[1,2] The measuring instruments are built according to the modular system and the measuring heads such as mixers, extruder etc. can be interchanged within a short time. Production processes like mixing, mastication, extrusion etc. can thus be simulated in a laboratory scale and followed by measurement.

The Plasticorder PL 2000 consists of a dynamometer unit, a data transfer interface and a computer. The dynamometer unit consists of the

Brabender torque dynamometer with electronic speed control with tacho generator feed back, stepless speed adjustment and digital speed display. The designed speed can be adjusted either manually at the dynamometer unit or can be fed via the computer. The dynamometer is combined with a high precision electronic strain gauge torque measuring unit moulded on a solid, tension–free base plate.

The data transfer interface with the standard serial communication port RS 232C and various microprocessors is an active link between the dynamometer unit and the computer. The data transfer interface series serves as an active support of the connected computer by a built in signal conditioning and control system with the following functions.

(1) Calibration of the torque and stock pressure measurements.

(2) Sequential scanning of the measuring values.

(3) Setting of speed control and all other functions of the system.

(4) Safety control and emergency switch–off.

(5) Enhancing the optimum temperature conditioning of the extruders by means of an additional standard serial communication port RS 422.

After installing the software, all further operations such as test runs, evaluation of measurements, or correlation analyses will be controlled by the computer. It is also possible to do the operation manually.

Brabender however uses measuring extruders and die heads, which are optimised for the individual experiments. Swell behaviour, surface quality, melt fracture, feeding characteristics, feeding rate measurements and many other criteria can be evaluated. This instrument serves the dual purpose of providing a constant torque drive for the extruder screw and simultaneously recording the torque on the screen. The pressure at the end of the screw and at the die has been monitored using Dynisco pressure transducers and suitable amplifier indicator set up. Iron constantan thermocouples were used to sense the melt temperature at the different regions of the screw and at the die. A "Servocar" strip chart was used to record these temperatures.

(a) Elastomers

In the case of elastomers, studies were done on a laboratory extruder attached to the above Brabender plasticorder model PL 2000 with an L/D ratio 10 and a compression ratio 1 and provided with a feeding roll. The sheets of thickness 1 mm of the compounds, prepared on the two roll mill, were cut into 10 mm wide strips, for feeding into the extruder. The feeding rates were adjusted by passing different number of layers of the strips on the feeding roll[3] and measured by the rate of output of the extrudate in milligrams per minute. The compounds were extruded at varying feeding rates at 20, 40, 60 and 80 rpms and at different temperatures. A round capillary die with L/D ratio of 15 with a

separate heater controller set up was used for the rubber extrusion studies.

(b) Thermoplastics

Experimental work was done on a laboratory extruder attached to a Brabender plasticorder model PL 2000 with an L/D ratio of 25 and a compression ratio of 2 and provided with a hopper for feeding. A vibratory feeder in conjunction with a voltage stabilizer was used for metering the solid pellets. A photograph of the plastic extruder attached to the Brabender plasticorder is shown in the Fig.2.1.

In the extrusion of elastomers and thermoplastics, the percentage of starvation at different feeding rates can be calculated by using the following equation:

$$\text{Percentag of starvation} = \frac{(\text{Flood feeding rate} - \text{Starve feeding rate}) \times 100}{\text{Flood feeding rate}}$$

Zero percentage starvation corresponds to the flood feeding rate in the extrusion of both elastomers and plastics.

The feeding rates were adjusted by changing the dimensions of the feed gap at the bottom of the hopper and measured by the rate of output of the extrudate[4] in milligrams per minute. The thermoplastics were extruded at varying feeding rates at 20, 40, 60 and 80 rpms and at different temperatures. A ribbon capillary die with L/D ratio 30 with a

Fig.2.1: Brabender PL 2000 with plastic extruder and die.

separate heater controller set up was used for the extrusion of thermoplastics.

2.3.2 Mixing and homogenisation

Using the mixing mill

Mixing and homogenisation of elastomers and compounding ingredients were done on a laboratory size (15x33 cm) two roll mill at a friction ratio of 1:1.2. The elastomer was given one pass through the nip (0.002x100)". Then it was given 2 passes through the nip of (0.002x10)" and allowed to band at the nip of (0.002x55)". The temperature of the rolls was maintained at 70±5°C during the mastication. After the nerve had disappeared, the compounding ingredients were added as per ASTM D 3184 (1980) and D 3182 (1982) in the order activators, fillers, accelerators and curing agents. Before the addition of accelerators and sulphur, the batch was thoroughly cooled.

After the completion of the mixing, the compound was homogenised by passing six times endwise through a tight nip and formally sheeted out at a nip of 3 mm. For the preparation of compounds to extrude, the elastomer was masticated to the suitable Mooney viscosity level and then the other additives were added as described above unless otherwise specified. Then it was sheeted out by passing through a 1 mm nip of the mixing mill.

2.3.3 Cure characteristics

The cure characteristics of the elastomers were determined using a Goettfert Elastograph model 67.85. It is a microprocessor controlled rotorless curemeter with a quick temperature control mechanism and well defined homogenous temperature distribution in the die or test chamber. In this instrument, a specimen of defined size is kept in the lower half of the cavity which is oscillated through a small deformation angle (+0.2°). The frequency is 50 oscillation per minute. The torque is measured on the lower oscillating die half. A typical elastograph cure curve is shown in Fig.2.2 and the following data can be taken from the torque-time cure.

i) Minimum torque: Torque obtained by the mix after homogenising at the test temperature before the onset of cure.

ii) Maximum torque: This is the torque recorded after the curing of the mix is completed.

iii) Scorch time: This is the time taken for attaining 10% of the maximum torque.

iv) Optimum cure time: This is the time taken for attaining 90% of the maximum torque.

The elastograph microprocessor evaluates the vulcanization curve and prints out these data after each measurement.

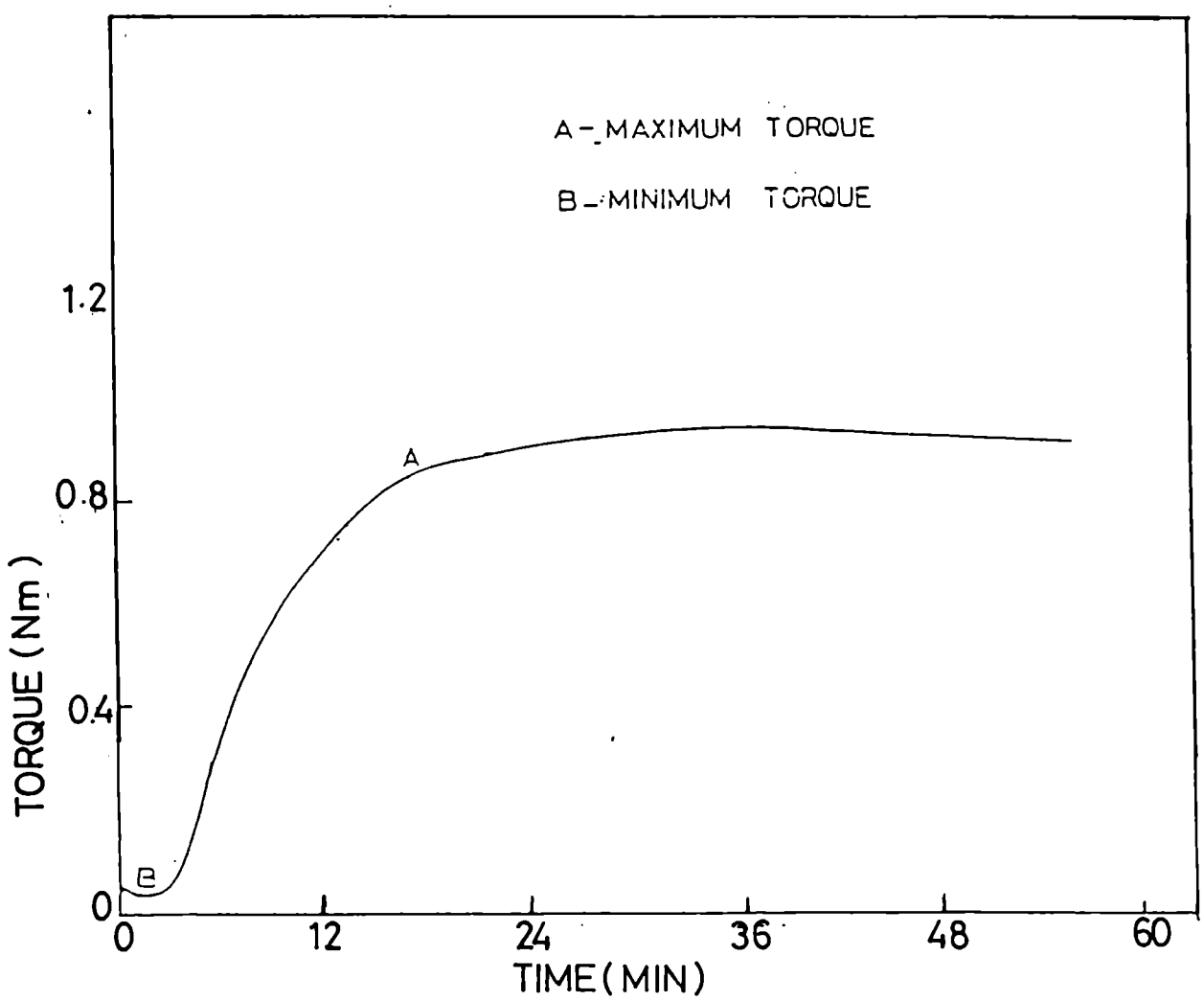

Fig.2.2: A typical cure curve of a rubber compound from elastograph.

2.3.4 Moulding of test specimens

The test specimens for determining the physical properties were prepared in standard moulds by compression moulding in an electrically heated press having (18x18 inch) platens at a pressure of 120 kg/cm^2 on the mould. The extruded rubber compounds were vulcanized upto their respective optimum cure times at 150°C unless otherwise specified. Mouldings were cooled quickly in water at the end of the curing cycle and stored in a cold and dark place for 24 hrs and were used for subsequent physical tests. For samples having thickness more than 5 mm (compression set, abrasion resistance etc.) additional curing time based on the sample thickness was given to obtain satisfactory mouldings.

In the case of thermoplastics the test specimens were punched out directly from the ribbon type extrudate both in the extrusion and transverse directions.

2.4 PHYSICAL TEST METHODS

At least five specimens per sample were tested for each property and the mean values are reported.

2.4.1 Tensile stress–strain behaviour

Tensile properties of the elastomers were determined accordingly to ASTM D 412 (1980) using dumb–bell specimens on a Zwick universal

testing machine (UTM) model 1445. All the tests were carried out at 28°C. Samples were punched out from compression moulded sheets using a dumb-bell die (C–type) both in the mill grain and transverse directions. The thickness of the narrow portion was measured by bench thickness gauge. The sample was held tight by the two grips, the upper grip of which was fixed. The rate of separation of the power activated lower grip was fixed at 500 mm/min for elastomeric specimens. The tensile properties of the thermoplastics were determined according to ASTM D 638 on the Zwick UTM model 1445. The rate of separation of the power activated lower grip was fixed at 50 mm/min. in this case. The tensile strength in N/mm^2 (MPa) and percentage elongation at break were evaluated and printed out after each measurement by the microprocessor.

2.4.2 Tear resistance

This test was carried out as per ASTM D 624 (1981) using unnicked, 90° angle test pieces. The samples of rubber were cut from the compression moulded sheet parallel to the mill grain direction. The test was carried out on a Zwick UTM model 1445. The speed of extension was 500 mm/min and the test temperature was 28°C. Tear resistance was measured in Newton per millimeter (N/mm).

2.4.3 Hardness

The hardness (Shore A) of the moulded samples was tested using Zwick 3114 hardness tester in accordance with ASTM D 2240 (1981) for rubber vulcanizates. The tests were performed on mechanically unstressed samples of 300 mm diameter and minimum 6 mm thickness. A load of 12.5 N was applied and the readings were taken after 10 seconds of indentation after firm contact had been established with the specimens. Hardness was expressed in 'Shore A' units.

2.4.4 Compression set

The rubber samples (6.25 mm thick and 18 mm diameter) in duplicate, compressed to constant deflection (25%) were kept for 22 hours in an air oven at 70°C according to ASTM D 395 (1982) method B. The samples were taken out from the compression set apparatus and cooled at room temperature for half an hour and the final thickness was measured. The compression set was calculated as follows:

$$\text{Compression set (\%)} = \frac{(t_o - t_1)100}{(t_o - t_s)}$$

where t_o and t_1 are the initial and final thickness of the specimen respectively and t_s the thickness of the spacer bar used.

2.4.5 Ageing studies

The ageing studies were carried out according to ASTM D 573. Dumb-bell samples for the evaluation of physical properties were

prepared and kept in an air oven at predetermined temperatures for specified periods. Physical properties like tensile strength and elongation at break were measured before and after ageing and the percentage retention of these properties was evaluated for assessing the effect of ageing.

2.4.6 Density

The densities of the polymer samples were measured by the method of displacement of liquid (ASTM D 792). In this method the weight of the specimen in air was first noted and then the specimen was immersed in water and its loss of weight, in water was determined. For specimens which were less denser than water, a sinker was used. The weight of the sinker in water was also measured. The density is given by,

$$\text{Density} = \frac{\text{Weight of specimen in air x Density of water}}{\text{Loss of weight in water}}$$

Density of water is taken as 1 gm/cc.

2.5 RHEOLOGICAL EVALUATION

Rheological studies of the polymeric solutions were done using a Brookfield viscometer (RVT model) according to ASTM D 1084. It consists of a rotating member which is usually a cylinder, driven by a synchronous motor through a beryllium copper torque spring. The viscous drag on the cylinder causes an angular deflection of the torque spring which is proportional to the viscosity of the fluid in which the disc is rotating. The

torque and therefore the viscosity is indicated by means of the pointer and scale. Viscosity was measured in centipoise. A range of speed of the discs and cylinders are available so that a wide range of viscosity may be covered.

Most of the polymeric solutions are non-Newtonian in nature and their viscosities decrease with increasing shear rate. In the present study the viscosity was measured at ambient temperature at 20 rpm for the thermoplastics and 10 rpm for elastomers.

2.6 THERMAL ANALYSIS

2.6.1 Thermogravimetric analysis (TGA)

The thermogravimetric analysis of the samples was done using a Du Pont-2000 Thermogravimetric analyser. About 10 mg of the sample was taken in a platinum crucible and the experiment was done in nitrogen atmosphere at a heating rate of 10°C/min. The weight loss of the sample was taken and then plotted against temperature.

2.6.2 Differential scanning calorimetry (DSC)

DSC thermograms were taken on a Mettler TA 3000 model at a heating/cooling rate 10°C/minute under nitrogen atmosphere as per ASTM D 3417 (1988). DSC yields peaks relating to endothermic and exothermic transitions, and show changes in heat capacity. The DSC

method also yields quantitative information relating to enthalpy changes in the polymer.

The DSC output plots energy supplied against average temperature. By this method, the area under the peak can be directly related to the enthalpy changes quantitatively and hence the degree of crystallinity.[5]

2.7 MORPHOLOGY STUDIES

2.7.1 Using optical microscope

The morphology of plastics was investigated using an optical microscope (Versanet–2 Union 7596). For optical microscopy samples were extruded and dissolved in solvents like p–xylene, toluene and thin films of the polymers were cast from these solutions. They were then cut into a convenient size and mounted on a microscopic slide. Photographs were taken at a magnification of 330.

2.7.2 Using polaroid land camera

Dispersion of ingredients in the compounded rubber stock was studied using photomicrographic technique. The technique employed an MP4 polaroid land camera with a magnification of 30.

Cured rubber sample was carefully microtomed on a razor blade guillotine and it was sandwiched between two rectangular sample holder.

The sample was then positioned under the microscope. Light grid was adjusted to shine across the sample parallel to the razor cut. The sample was viewed through a reflux viewer to scan its surface. After assuring maximum sample illumination, black and white polaroid photographs were taken.

2.7.3 Using scanning electron microscope (SEM)

Scanning electron microscope was first introduced in 1965 and it has since become a very useful tool in polymer research for studying morphology.[6-8] SEM Stereo scan 250 MK3 Cambridge instrument was used to investigate the morphology of fractured surfaces. In this technique an electron beam is scanned across the specimen resulting in back scattering of electrons of high energy, secondary electrons of low energy and X-rays. These signals are monitored by detectors and magnified. An image of the investigated microscopic region of the specimen is thus photographed.

If the specimen under investigation is not a good conductor, it should be coated with a thin layer of conducting material like platinum or gold. This is done by placing the specimen in a high vacuum evaporator and vapourising the conducting material held in a tungsten basket (vacuum dispersion).

The SEM observations reported in the present study as per ASTM D 3417 (1988) were made on the fracture surfaces of tensile test specimens. The fracture surfaces of the samples were carefully cut without disturbing the surface. These surfaces were then sputter coated with gold within 24 hours of testing. The SEM observations were made within 24 hours of coating. The gold coated samples were kept in a desiccator before the SEM observations were made. The shapes of the tensile test specimens, direction of the applied force and the portions from where the surfaces have been cut out for SEM observations are shown in Fig.2.3.

2.8 CHEMICAL TEST METHODS

2.8.1 Determination of chemical crosslink density

The concentration of chemical crosslinks was estimated from the equilibrium swelling data as follows. Samples of approximately 1 cm diameter, 0.20 cm thickness and 0.20 gm weight were punched out from the central portion of the compression moulded sheet and allowed to swell in solvent (toluene or benzene depending on the nature of the rubber). The swollen samples were taken out from the solvent after equilibrium swelling and weighed.

The deswollen weight of the samples were taken after drying the samples in an oven for 1 hour. The volume fraction of rubber (V_r) in the

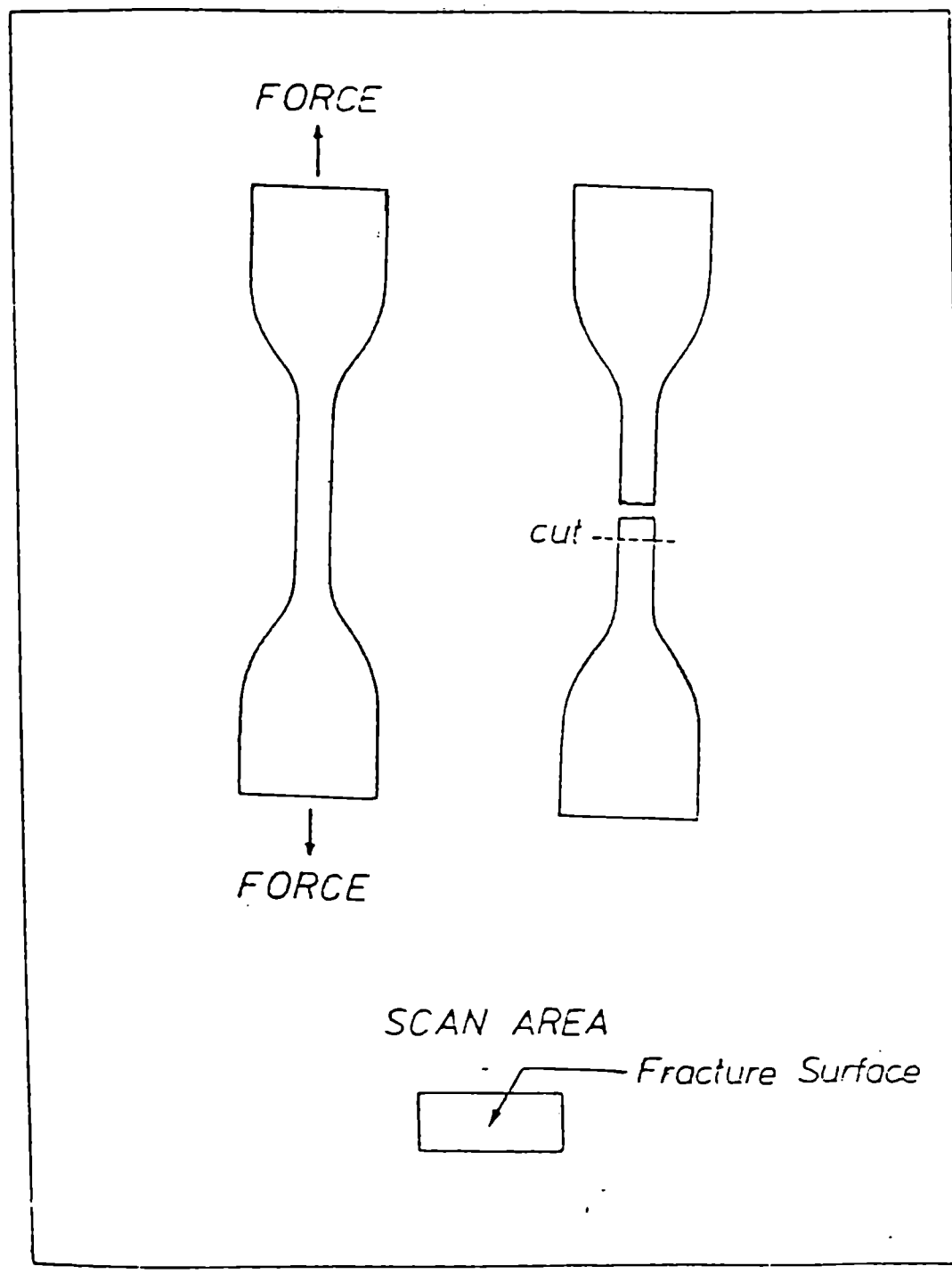

Fig.2.3: SEM scan area of the tensile fracture surface.

swollen network was then calculated by the method reported by Ellis and Welding[9] from the following equation

$$V_r = \frac{(D—FT)\,\rho_r^{-1}}{(D—FT)\,\rho_r^{-1} + A_o\,\rho_s^{-1}}$$

where

T = weight of the test specimen

D = deswollen weight of the test specimen

F = weight fraction of insoluble components

A_o = weight of the absorbed solvent corrected for the swelling increment

ρ_r = density of rubber and ρ_s = density of solvent

The value of ρ_r and ρ_s taken were:

ρ_r(NR) = 0.921 gm/cm^3 ρ_s(Toluene) = 0.886 gm/cm^3

ρ_r(SBR) = 0.940 gm/cm^3 ρ_s(Benzene) = 0.875 gm/cm^3

ρ_r(IIR) = 0.93 gm/cm^3

The total crosslink density ($\frac{1}{2}M_c$) expressed in gram mol per cubic centimeter (gm mol/cc) was then determined from V_r using the Flory–Rehner equation.[10,11]

$$-[\ln(1 - V_r) + V_r + \chi V_r^2] = \frac{\rho_r V_s (V_r)^{1/3}}{M_c}$$

where

V_s = molar volume of solvent

For toluene V_s = 106.2 cc/mole

For benzene V_s = 90 cc/mole

χ = parameter characteristic of interaction between rubber and solvent

Values of parameter χ taken for calculations[12,13] were the following.

For

NR–Toluene, $\chi = 0.42$

SBR–Toluene, $\chi = 0.32$

IIR–Benzene, $\chi = 0.314$

In the case of carbon black filled vulcanizates, the value of V_r was converted into V_{ro} (the value V_r would have had in the absence of black) according to Cunneen and Russel.[14]

$$\frac{V_{r_o}}{V_r} = ae^{-z} + b$$

Here 'a' and 'b' are constants characteristic of the system and 'z' is the weight fraction of the filler in the vulcanizate. The values for a and b for HAF black filled system are a = 0.56 and b = 0.44. The values of V_{r_o} were then substituted in the Flory–Rehner equation in the place of V_r to obtain the crosslink density $\frac{1}{2}M_c$.

2.8.2 Swelling index determination

Rubber samples of about 0.5 gm weight were cut from the compounds and kept in a suitable solvent (toluene or benzene depending on the nature of the rubber) at laboratory temperatures for 36 hours. The solvent used for NR and SBR was toluene and that used for IIR was benzene. The samples were taken out, quickly dried with a filter paper and the swollen weight was found. Then the swollen samples were dried in a vacuum oven at 60°C for 12 hours, and the deswollen weight was noted. The ratio of change in weight was calculated and expressed as swelling index.

$$\text{Swelling index} = \frac{\text{(Swollen weight - Deswollen weight)}}{\text{Initial weight}}$$

2.8.3 Bound rubber content determination

About 0.2 gm of the compound was cut into small pieces and placed into a stainless steel wire mesh cage of known weight. The cage was then immersed in 25 ml of solvent for seven days at room temperature and the solvent was renewed after three days. The solvents used for the bound rubber determination was toluene for NR & SBR and benzene for IIR. After extraction, the rubber and the cage were dried for one day in air at room temperature and then for 24 hours in an oven at 105°C. The percent bound rubber of the polymer (R_B) was then calculated as described by Wolff et al.[15] according to the following equation:

$$R_B = \frac{W_{fg} - W\,[m_f/(m_f + m_p)]\ x\ 100}{W[m_p/(m_f + m_p)]}$$

where,

W_{fg} is the weight of the carbon black and gel, m_f, the weight of the filler in the compound, m_p, the weight of the polymer in the compound and W the weight of the specimen.

References

1. Z.Bartha, P.Erdos and J.Matis, Int. Polym. Sci. Technol., 10(6), 50 (1983).
2. J.E.Goodrich and R.S.Porter, Polym. Eng. Sci., 7, 45 (1967).
3. R.Brozoskowski, J.L.White, F.C.Weissert, N.Nakajima, and K.Mini, Rubber Chem. Technol., 59, 634 (1986).
4. G.Menges and J.Muller, Plastverarbeiter, 21, 305 (1970).
5. T.Shindo and T.Vryu, Journal of Polym. Sci. Part A, Polymer Chemistry, 30, 363 (1992).
6. R.J.White and E.L.Thomas, Rubber Chem. Technol., 57, 457 (1985).
7. L.Engel, H.Klingele, G.W.Ehrenstein and H.Schaper, "An Atlas of Polymer Damage", Prentice Hall, New Jersey (1981).
8. E.Balcerzylk, J.Hochstim and S.Wlodarczyk, Int. Polym. Sci. Technol., 12, 121 (1985).
9. B.Ellis and G.N.Welding, "Techniques of Polymer Science", Society of Chemical Industry, London, 17, 46 (1964).
10. P.J.Flory and J.Rehner, J. Chem. Phys., 11, 512 (1943).
11. P.J.Flory and J.Rehner, J. Chem. Phy., 11, 521 (1943).
12. C.J.Sheelan and A.L.Basio, Rubber Chem. Technol., 39, 149 (1966).

13. Ashagom, Rubber Chem. Technol., 59, 187 (1986).

14. J.I.Cunnen and R.M.Russel, Rubb. Chem. Technol., 43, 1215 (1970).

15. S.Wolff, Meng-Jiauwang and Ewe-Hongton, Rubb. Chem. Technol., 66, 163 (1993).

CHAPTER 3

EFFECT OF FEEDING RATE ON THE TECHNICAL PROPERTIES OF GUM NR, SBR AND IIR VULCANIZATES

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EFFECT OF FEEDING RATE ON THE TECHNICAL PROPERTIES OF GUM NR, SBR AND IIR VULCANIZATES

3.1 INTRODUCTION

In a conventional extruder, the extrusion rate is a function of the screw geometry for a given set of operating conditions.[1] However, if the rate of feeding and hence the output rate can be made an independent operating variable, there are many advantages.[2-5] Russel J. Nichols and George A.Kruder[6] have listed the potential advantages of starve feed metering. Their results reveal that the screw torque requirement under starved conditions is considerably less compared to normal operations. This imparts greater versatility in extruder operations.[7-9] For example, tough materials requiring a high screw torque capacity can be successfully handled with the same screw under starved conditions. Isherwood et al.[10] have reported various other beneficial effects of starve feeding.

Because of the high viscosity (greater than 100 Ns/m^2) that is characteristic of polymer melts, a significant amount of viscous heat can be generated in flows that are subjected to high shear rates in extrusion.[11] Moreover, polymers have low thermal conductivities ensuring that high shear operations result in an increase in temperature of the polymer.

Because polymers have limited thermal stabilities, extrusion is limited to low shear operations or regions of limited high shear as in starved extrusion. Such limited high shear regions usually involve the flow of a thin polymer melt over a large surface area for maximum heat transfer and thereby resulting in maximum uniform mixing as shown by Spencer et al.,[12] G.Pinto et al.[13] and then by D.M.Bigg et al.[14]

Since there can be large viscous heat generation in flood feeding and force feeding followed by low internal heat transfer significantly large temperature differences may occur within the flowing material, large enough to affect its rheological behavior and induce degradations. Thus starve feeding is likely to result in improved mechanical properties due to lower and/or uniform shear resulting in lower heat generation, better thermal homogeneity, and preferential orientation of the molecules. Hence properly controlling the feeding rate in the extrusion of polymers may be an important way of controlling their mechanical properties. In the case of elastomer compounds varying the feeding rates may lead to changes in the curing behavior and hence may result in different vulcanizate structures.

This study has been undertaken to determine the effect of feeding rate on the mechanical properties of gum NR, SBR and IIR vulcanizates.

3.2 EXPERIMENTAL

Studies were done on a laboratory extruder attached to a Brabender Plasticorder model PL 2000 with an L/D ratio of 10 and a compression ratio of 1 and provided with a feeding roll. The formulations of the gum compounds of NR, SBR and IIR selected for the study are shown in Table 3.1.

Compounds were prepared on a laboratory two-roll mill according to ASTM Standards. The compounds were sheeted out by passing through a 1 mm nip of the mixing mill. The sheets were cut into 10 mm strips for feeding into the extruder. The feeding rates were adjusted by placing different number of layers of the strips on the feeding roll[15] and measured by the rate of output of the extrudate.[16] The compounds were extruded at varying feeding rates mainly in the starve fed regions at 20, 40, 60 and 80 rpm and at different temperatures. The feeding rates were then increased to flood fed level and force fed level, at the above rpms and temperatures. The torque values corresponding to various feeding rates at above rpms and temperatures were noted.

The cure curves of the NR, SBR and IIR gum compounds after extrusion were taken on a Goettfert Elastograph model 67.85 according to ASTM standards at 150°C in the case of NR & SBR compounds and at 170°C in the case of IIR compounds. The extruded samples were vulcanized

Table 3.1: Formulations of the compounds

	NR gum compound	SBR gum compound	IIR gum compound
NR	100	--	--
SBR	--	100	--
IIR	--	--	100
Zinc oxide	5.0	4.0	4.0
Stearic acid	2.0	1.5	2.0
Antioxidant (Pilflex-13)	1.0	1.0	1.0
Dibenzthiazyl disulphide (MBTS)	0.6	--	0.5
Tetramethyl thiuram disulphide (TMTD)	--	0.25	1.0
N–cyclohexyl–2–benzthiazyl sulphenamide (CBS)	--	0.8	--
Sulphur	2.5	2.0	1.5

up to their optimum cure times (the time required for attaining 90% of the maximum torque) in an electrically heated laboratory hydraulic press. The moulded samples were then cooled by immersing in water and dumb-bell specimens were cut out of the sheets in the milling/extrusion and transverse directions for tensile testing. The tensile properties of the vulcanizates were measured using a Zwick universal testing machine model 1445 at an extension rate of 500 mm/min as per ASTM standards. Angular test specimens were punched out of the compression moulded sheets and tear strength of selected vulcanizates was measured on the Zwick UTM. Samples for compression set and hardness were moulded and tested as per relevant ASTM standards.

The ageing resistance of selected vulcanizates was studied after ageing the samples at 100°C for 48 hrs in a laboratory air oven and then measuring the retention in relevant properties.

The percentage of starvation[10] at different levels was calculated by noting the corresponding starve feeding rate and the flood feeding rate as described in the chapter 2.

Temperature and flow rate fluctuations at certain starvation levels, flood feeding and force feeding levels during extrusion were noted. The

densities of a few sets of starve fed, flood fed and force fed samples of NR, SBR and IIR extruded gum vulcanizates were measured.

The swelling index of the NR and SBR vulcanizates was measured by equilibrium swelling in toluene and in the case of IIR vulcanizates by equilibrium swelling in benzene according to the following equation

$$\text{Swelling index} = \frac{\text{Swollen weight} - \text{Deswollen weight}}{\text{Initial weight}}$$

The average chemical crosslink density of a few sets of starve fed, flood fed and force fed samples of NR, SBR and IIR vulcanizates was estimated from equilibrium swelling data.[17] The crosslink density $\frac{1}{2}M_c$ was determined from V_r using the Flory-Rehner[18,19] equation. The viscosity values of extruded NR, SBR and IIR compounds were measured by using a Brookfield viscometer. The TGA curves of starve fed, flood fed and force fed compounds of NR, SBR and IIR were taken on a thermogravimetric analyser, model Du-Pont-2000.

3.3 RESULTS AND DISCUSSION

3.3.1 Torque

Figure 3.1 shows the variation of torque with feeding rate for NR, SBR and IIR at 80°C for different rpms of 20, 40, 60 and 80. It is found that

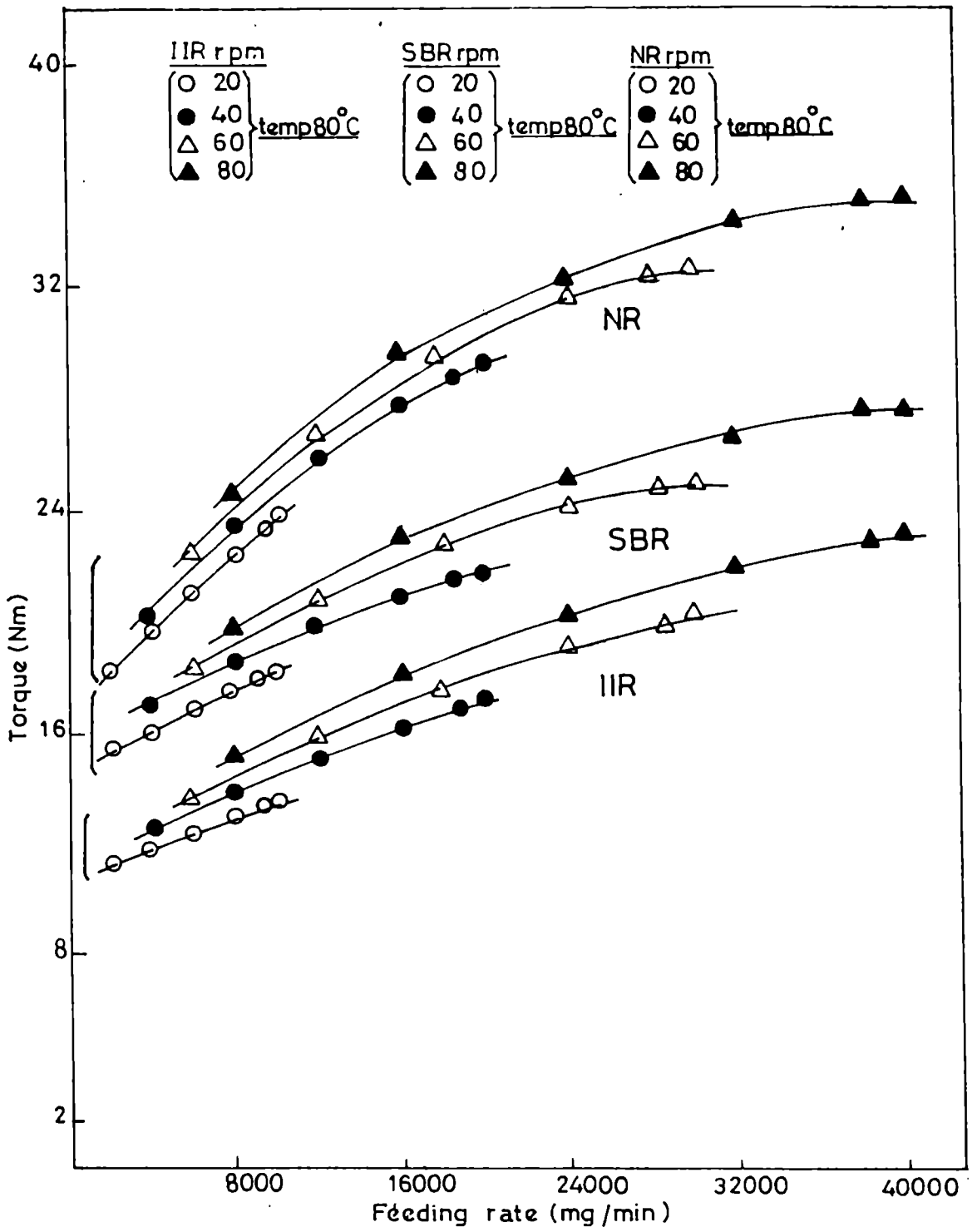


Fig.3.1: Variation of torque in the extrusion of gum NR, SBR and IIR compounds with feeding rate at different rpm.

the extrusion torque gets progressively reduced with increase in the starvation level. The percentage reduction in torque between the flood feeding point and the lowest feeding point is upto 33%.

Figure 3.2 shows the variation of torque with feeding rate for NR, SBR and IIR at different temperatures and at a fixed rpm of 40. Here also the extrusion torque gets progressively reduced with increase in starvation level. The percentage reduction in torque between the flood feeding point and the starve feeding point is upto 37% in the extrusion of NR, SBR and IIR gum vulcanizates.

In the above cases, beyond the flood feeding point, torque again increases at the force feeding level. From the figures 3.1 and 3.2, it can be concluded that the torque required for extrusion can be substantially brought down by operating in the starved region or employing higher temperatures. The variation of reduction in torque with percentage of starvation at two different rpms and two different temperatures is shown in the Table 3.2.

3.3.2 Mechanical properties

3.3.2.1 Tensile properties

Figure 3.3 shows the variation of tensile strength with feeding rate for NR, SBR and IIR gum vulcanizates in the milling/extrusion direction at

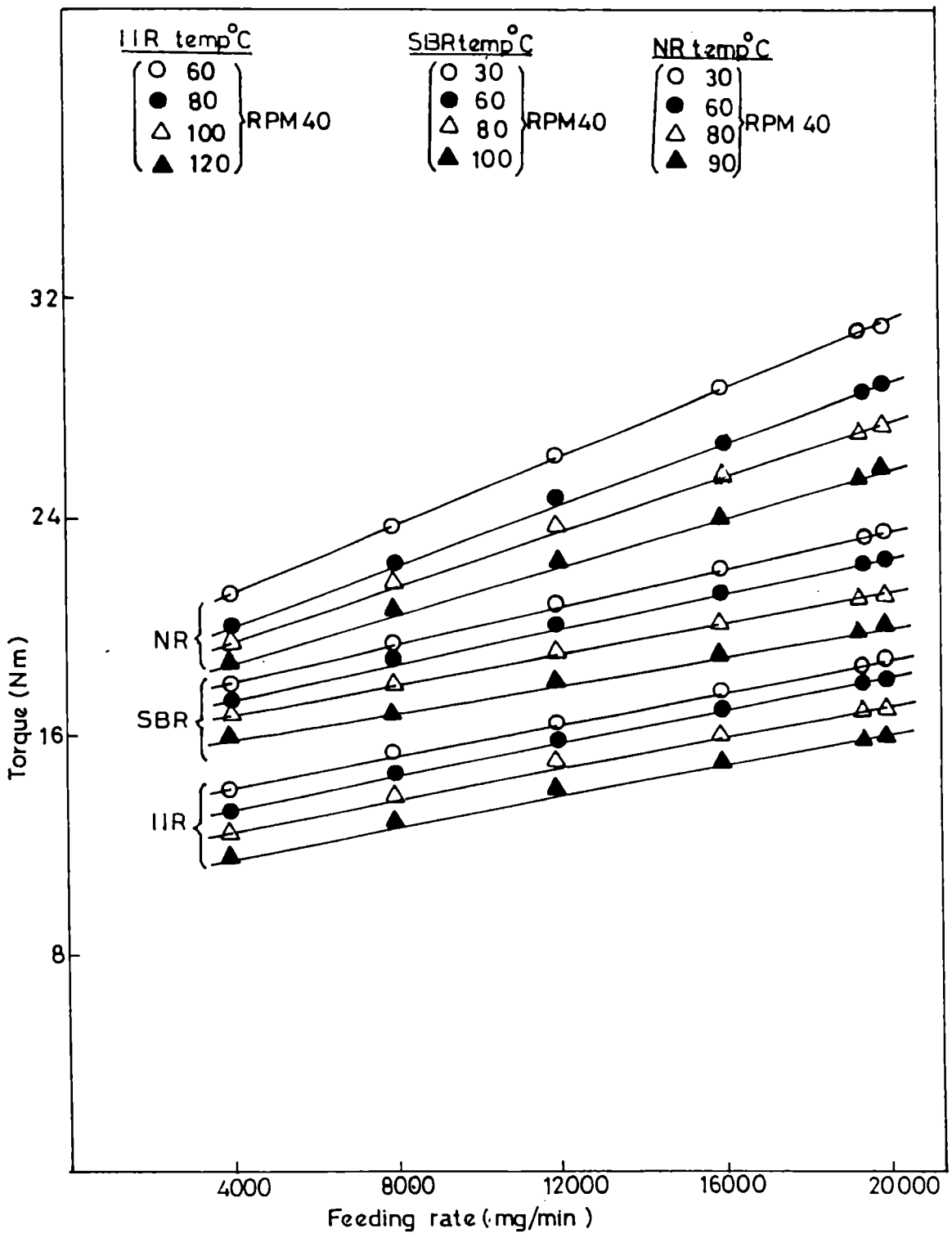


Fig.3.2: Variation of torque in the extrusion of gum NR, SBR and IIR compounds with feeding rate at different temperatures.

Table 3.2: Variation of the percentage reduction in torque with percentage of starvation of gum NR, SBR, IIR compounds

% Starvation	% Reduction in Torque at 20 rpm at 80°C			% Reduction in Torque at 80 rpm and 80°C			% Reduction in Torque at 40 rpm at 60°C			% Reduction in Torque at 40 rpm at 100°C		
	NR	SBR	IIR	NR	SBR	IIR	NR	SBR	IIR	NR	SBR	IIR
80	27.8	29.5	33.0	28.0	30.1	31.5	25.0	27.4	30.2	31.0	32.2	37.1
50	18.8	22.2	25.8	23.9	25.0	27.3	18.2	19.3	23.5	24.5	26.3	28.7
30	14.5	15.9	18.8	14.2	15.5	16.6	14.1	15.0	16.9	17.1	18.5	20.1
10	12.0	12.8	14.2	11.0	11.5	12.0	11.0	12.0	12.8	12.0	13.1	15.2
0 (Flood feeding)	--	--	--	--	--	--	--	--	--	--	--	--

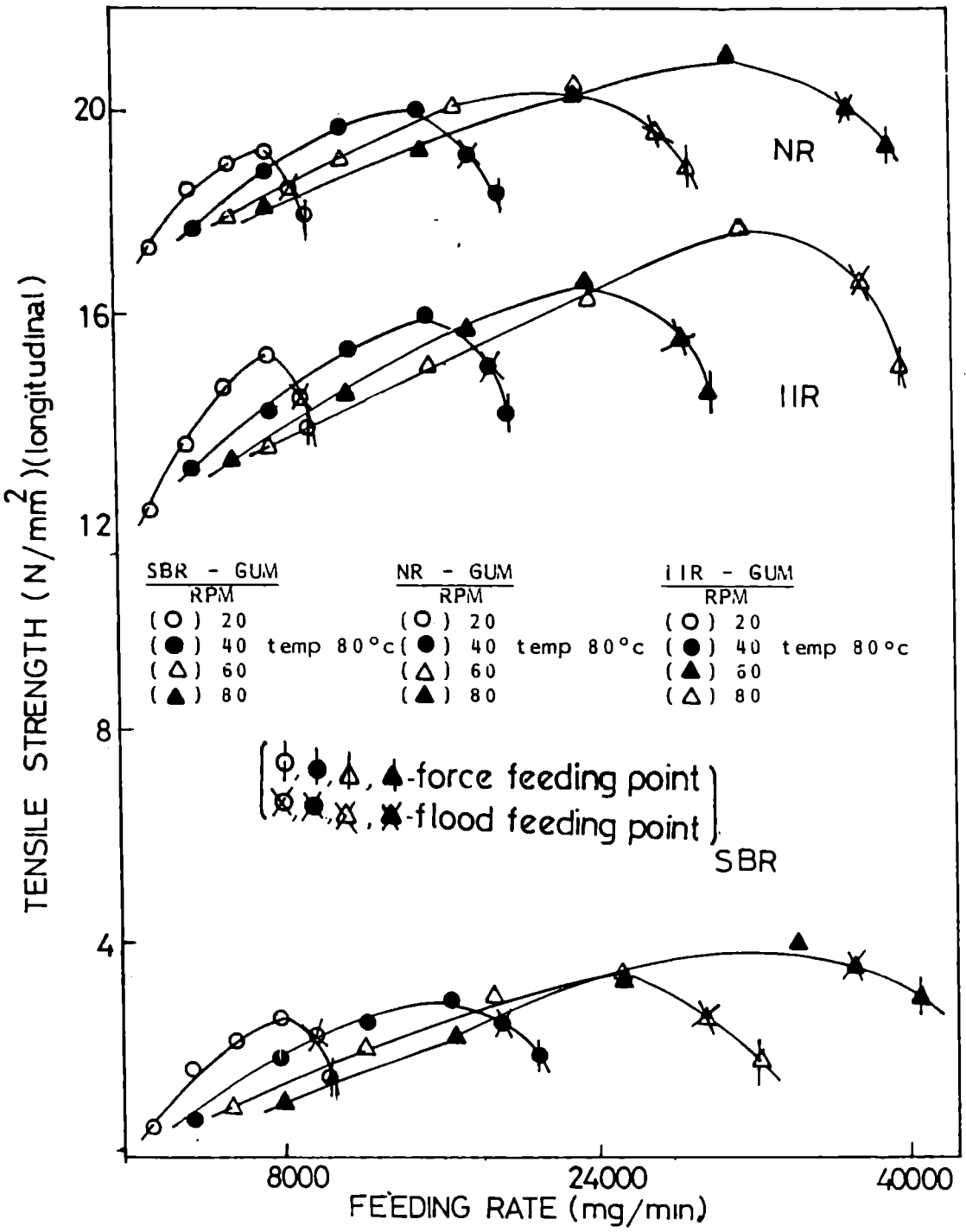


Fig.3.3: Variation of tensile strength of gum NR, SBR and IIR vulcanizates with feeding rate at different rpm in the milling/extrusion direction

different rpms at 80°C. The maximum feeding rate in each curve in the figure corresponds to the force fed point. The feeding rate just below force fed point in the curve represents flood feeding point and the other feeding rates are in the starve fed region.

It is found that irrespective of rpm the tensile strength initially increases with feeding rate, reaches a maximum value and thereafter decreases in the case of NR, SBR and IIR gum vulcanizates. This shows that there is a particular feeding rate in the starved region, which results in maximum tensile strength. Isherwood et al.[10] suggests that the starve feeding results in looser packing of the material in the channel which allow greater bed mobility. Hence local high temperatures are not built up at the bed-to-barrel interface as found when the bed is densely compacted. In addition, the bed is more flexible and so does not snap under the influences of forces on it giving a smoother profile as shown by Fenner et al.[20] So the improvement at a low starvation level is possibly due to improved uniformity in temperature of the compounds. Moreover, additional bed mobility may result in more uniform mixing.[21] Erwin[22] has shown that elongational flow can be more effective than shear flow for maximizing mixedness in a given time frame as occurred in starved extrusion at a particular level of starvation. Further, lower shear breakdown and preferential orientation of the molecules may be the other reasons for the

higher tensile strength at this feeding rate.[23] The preferential orientation effect is clearly seen from the higher difference between the tensile strength measured in the milling/extrusion and transverse directions in this case (Figs.3.3 and 3.4). The preferential orientation effect is more pronounced in NR vulcanizates than that of SBR and IIR. It may be due to the crystalline nature of NR compared to SBR and IIR. After the starve feeding point at which maximum tensile strength is observed, the tensile strength decreases with feeding rate at the flood feeding point and force feeding point.

In flood feeding and mainly in force feeding comparatively non-uniform higher shear is operating and hence may result in non-uniform heat transfer and hence non-uniform temperature distribution within the material. Generally the heat transferring efficiency of conventional screws is decreased by phenomena associated with the existence of relatively thick melt layers in flood feeding and force feeding, that are in contact with the solid bed namely, the melt pool and the melt film at the screw surface. Their presence introduces an appreciable heat transfer resistance and, even more importantly, may cause the solid bed to break up frequently and hence it results in non-uniform temperature distribution.[24] So thermal homogeneity is not easily attained as in the case of starve feeding. As a result of this non-uniform temperature and shear history, the extrudate properties are progressively affected in flood feeding and in force feeding.

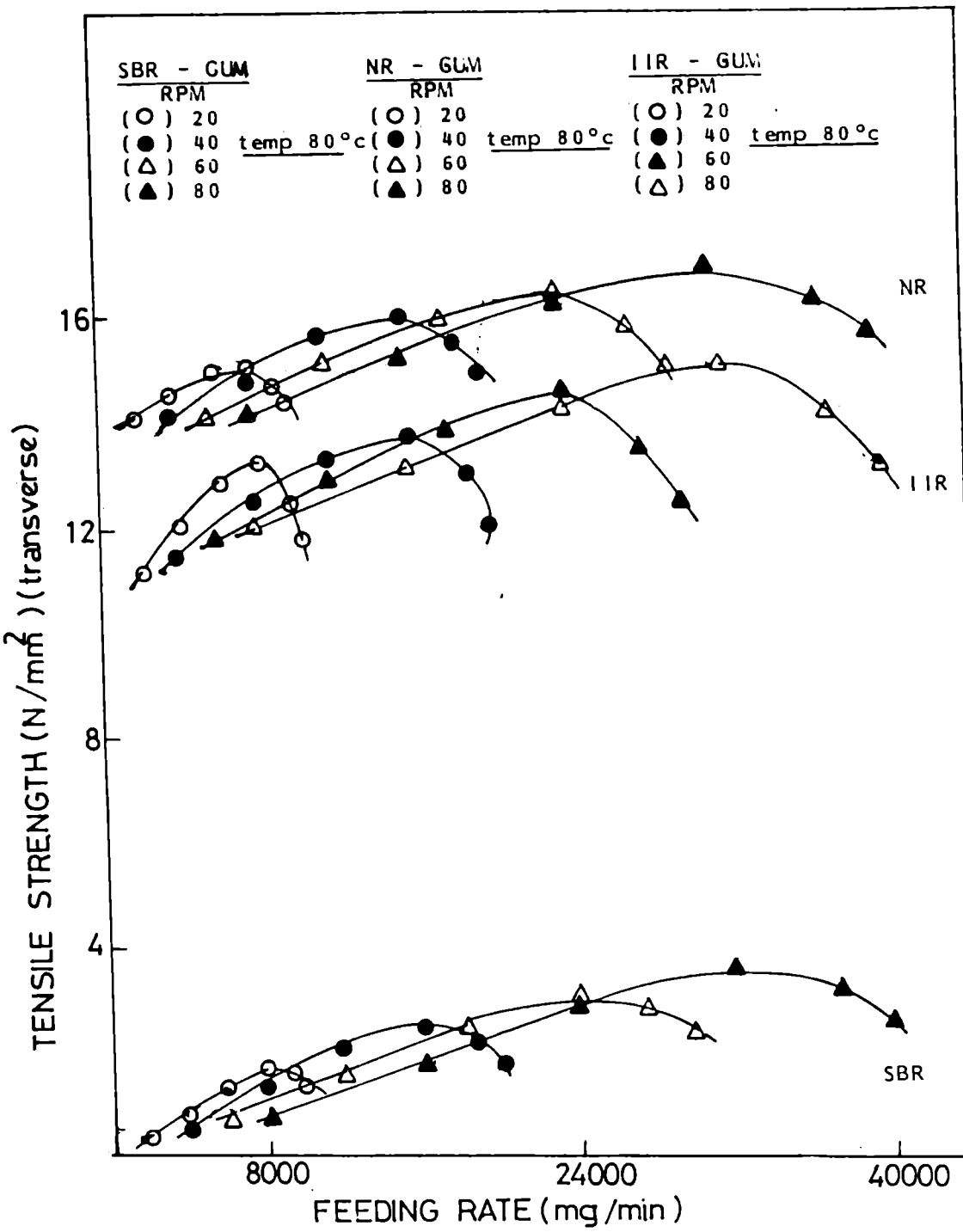


Fig.3.4: Variation of tensile strength of gum NR, SBR and IIR vulcanizates with feeding rate at different rpms in transverse direction.

Figures 3.5 and 3.6 show the variation in elongation at break of NR, SBR and IIR vulcanizates with feeding rate in milling/extrusion and transverse directions at different rpms. As in the case of tensile strength unimodel curves are obtained for each rpm. This further shows the efficiency of starved extrusion in getting maximum physical properties. The simultaneous increase in the tensile strength and elongation at break of the extrudates at a particular level of starvation indicate the uniform shear and lower mechanical break-down at this feeding rate.[25]

Figures 3.7 and 3.8 show the variation in tensile strength of NR, SBR and IIR gum vulcanizates with feeding rate in the milling/extrusion and transverse directions at different temperatures at a fixed rpm. In the case of NR, the tensile strength improves with the temperature, when the temperature is raised from 30°C to 90°C, in the case of SBR, the strength improves with the temperature from 60°C to 100°C and in the case of IIR, the strength improves with the temperature from 60°C to 120°C, showing that deterioration due to thermal degradation is not serious in these ranges respectively. But the strength at 100°C is less than at 90°C in the case of NR, the strength at 120°C is less than at 100°C in the case of SBR and the strength at 140°C is less than at 120°C in the case of IIR vulcanizates showing the onset of degradation. In the case of IIR, thermal degradation takes place comparatively at a higher temperature than that takes place in

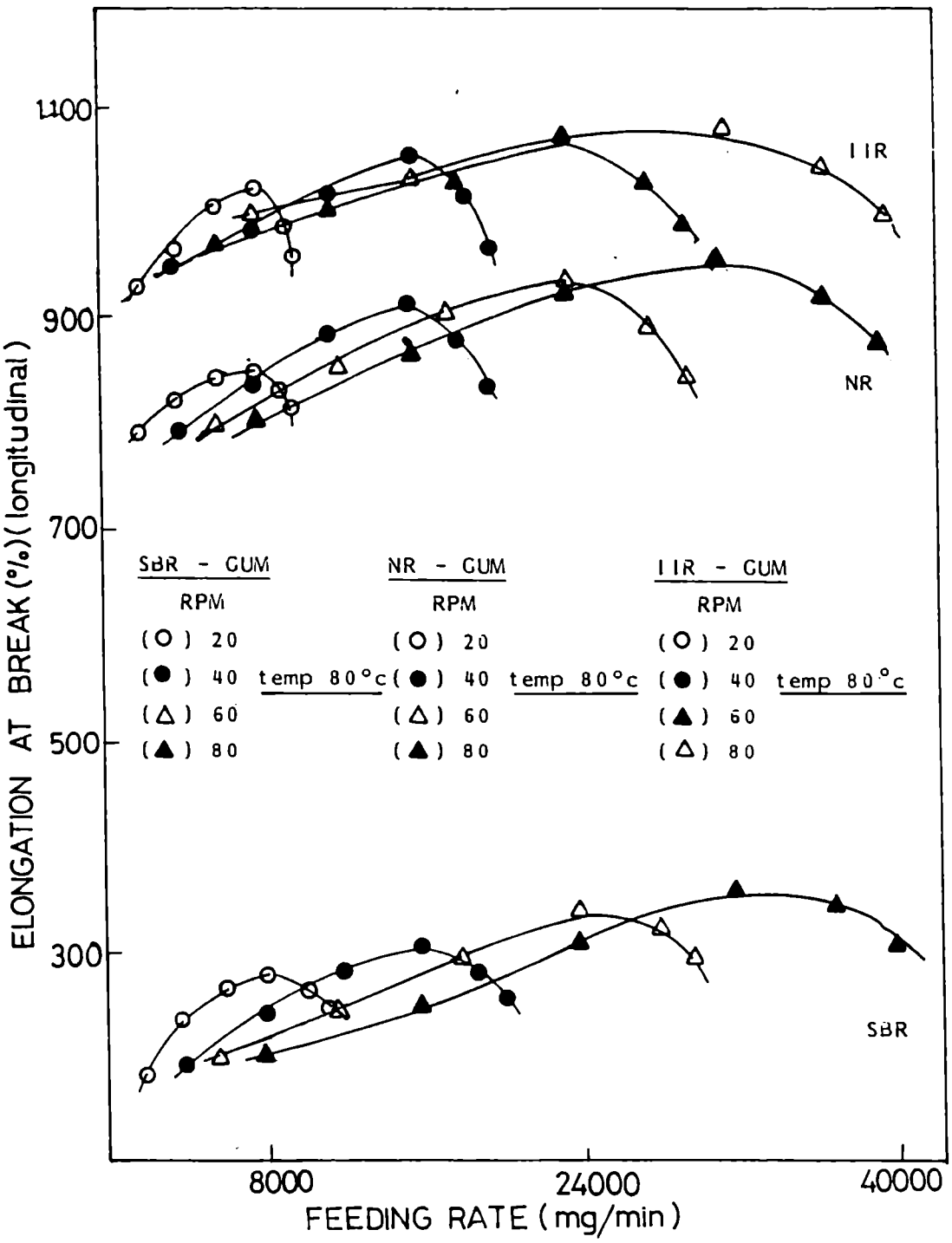


Fig.3.5: Variation of elongation at break of gum NR, SBR and IIR vulcanizates with feeding rate at different rpms in the milling/extrusion direction.

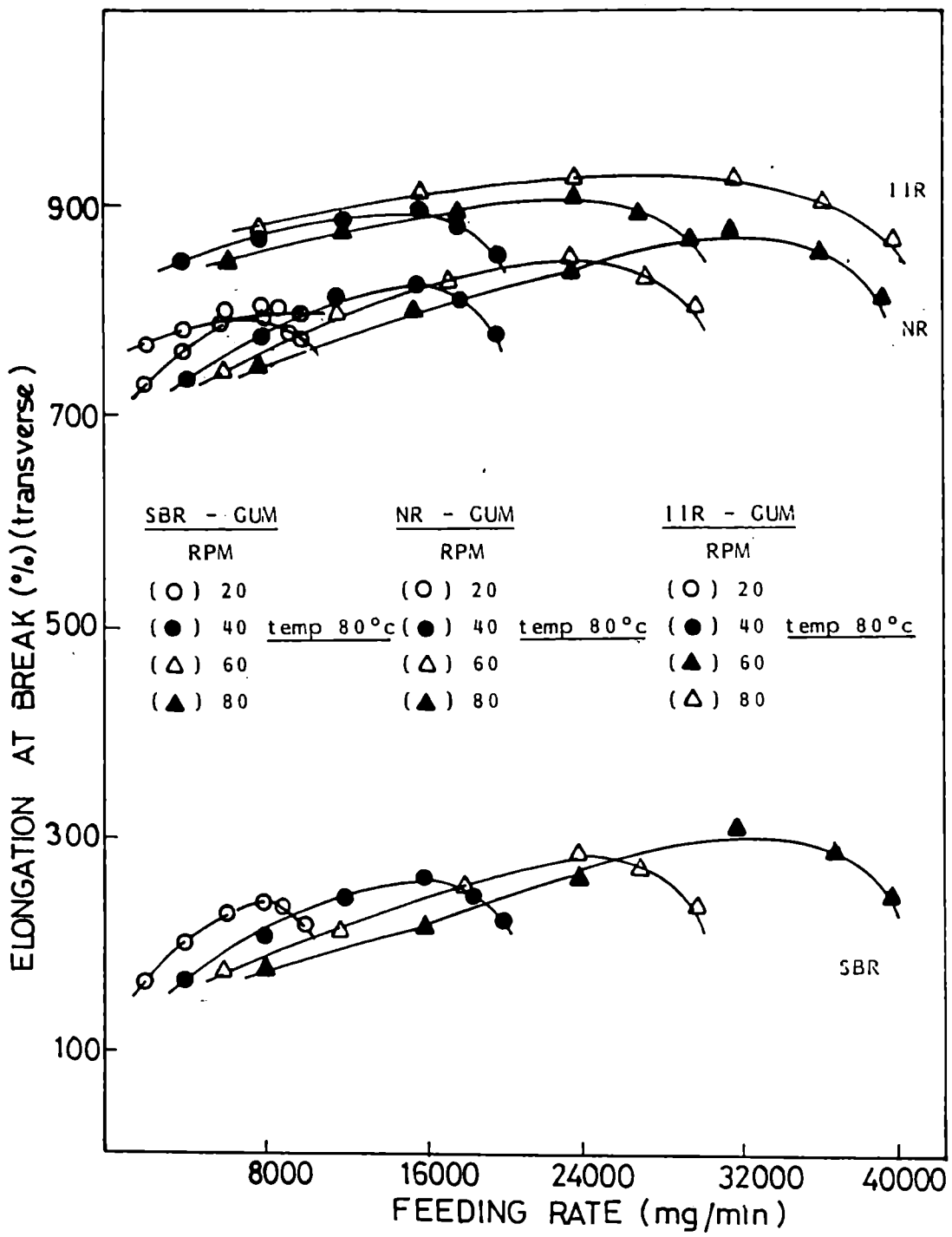


Fig.3.6: Variation of elongation at break of gum NR, SBR and IIR vulcanizates with feeding rate at different rpms in the transverse direction.

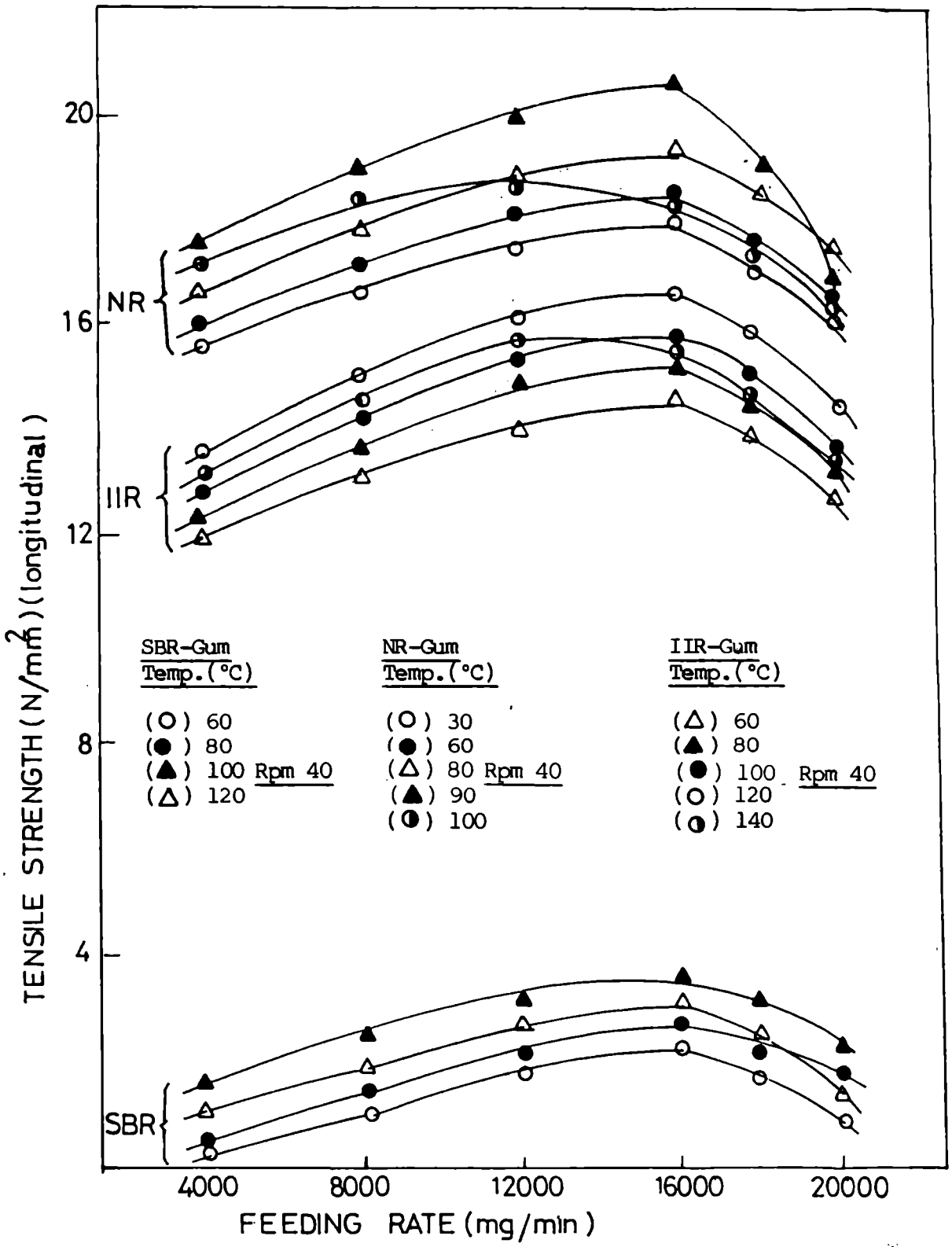


Fig.3.7: Variation of tensile strength of gum NR, SBR and IIR vulcanizates with feeding rate at different temperatures in the milling/extrusion direction.

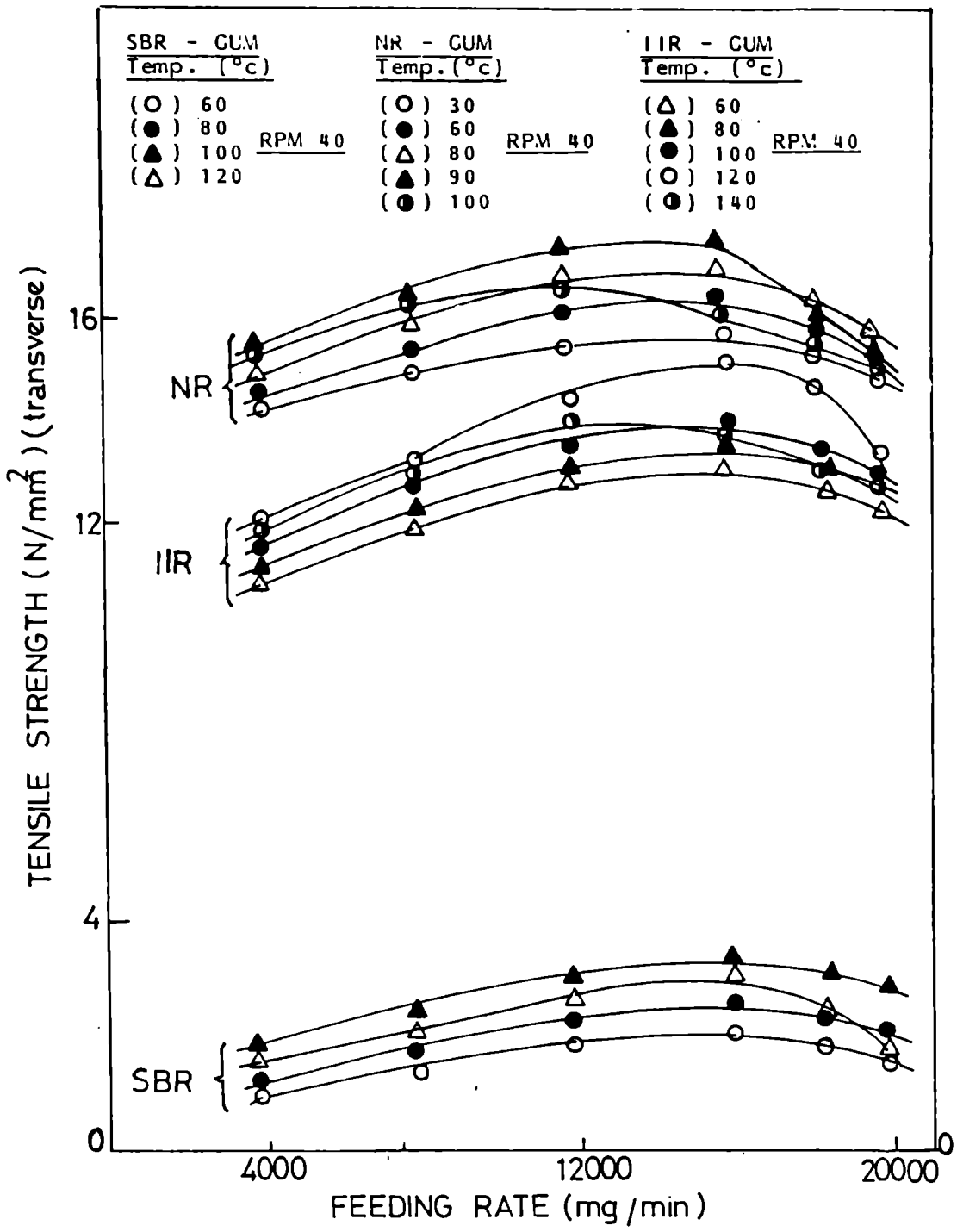


Fig.3.8: Variation of tensile strength of gum NR, SBR and IIR vulcanizates with feeding rate at different temperatures in the transverse direction.

the case of NR and SBR showing the superior thermal resistance of IIR vulcanizates.[26] In the case of SBR thermal degradation takes place at a higher temperature than that takes place in the case of NR since SBR is more thermally stable than NR.

It is found that the effect of starve feeding at lower temperatures is more pronounced in the case of NR gum extruded vulcanizates than that of SBR and IIR gum vulcanizates. It may be due to the more heat sensitive nature of natural rubber compared to SBR and IIR. It may also be noted that in the case of NR, the strength at 90°C in higher feeding rate/shear rate region is less than that at 80°C. This shows that even at 90°C, thermal degradation occurs particularly at the higher shear rates used in the study. At every temperature, the strength increases with feeding rate reaches a maximum and decreases thereafter. As before the maximum occurs just below the flood feeding (normal feeding) rate, in the range 30–90°C and further down at 100°C in the case of NR. In the case of SBR the maximum strength is observed just below the normal feeding rate in the range 60–100°C and further down at 120°C and in the case of IIR maximum strength occurs just below the normal feeding rate in the range 60–120°C and further down at 140°C.

Figures 3.9 and 3.10 show the variation of elongation at break of NR, SBR and IIR vulcanizates with feeding rate at different temperatures

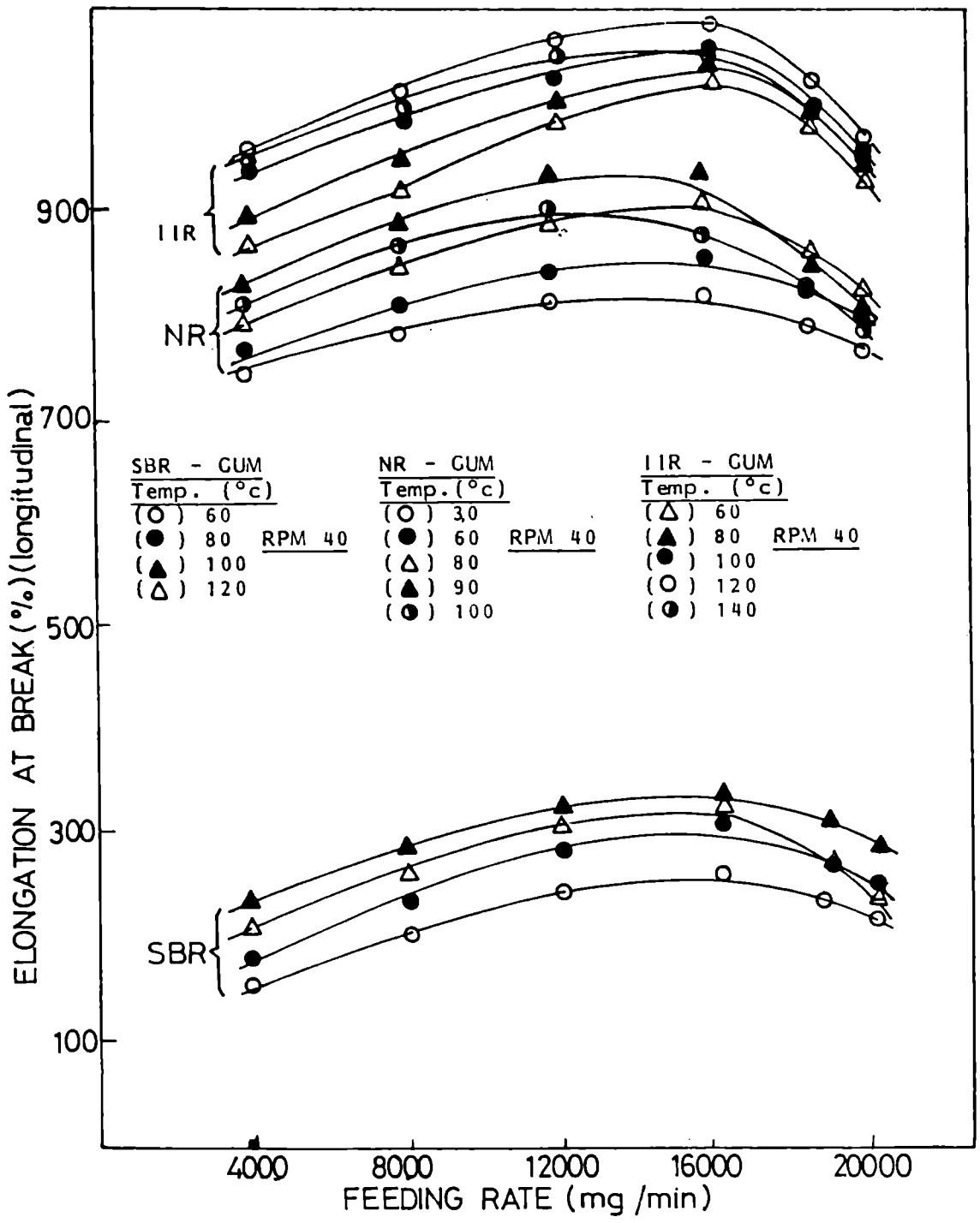


Fig.3.9: Variation of elongation at break of gum NR, SBR and IIR vulcanizates with feeding rate at different temperatures in the milling/extrusion direction.

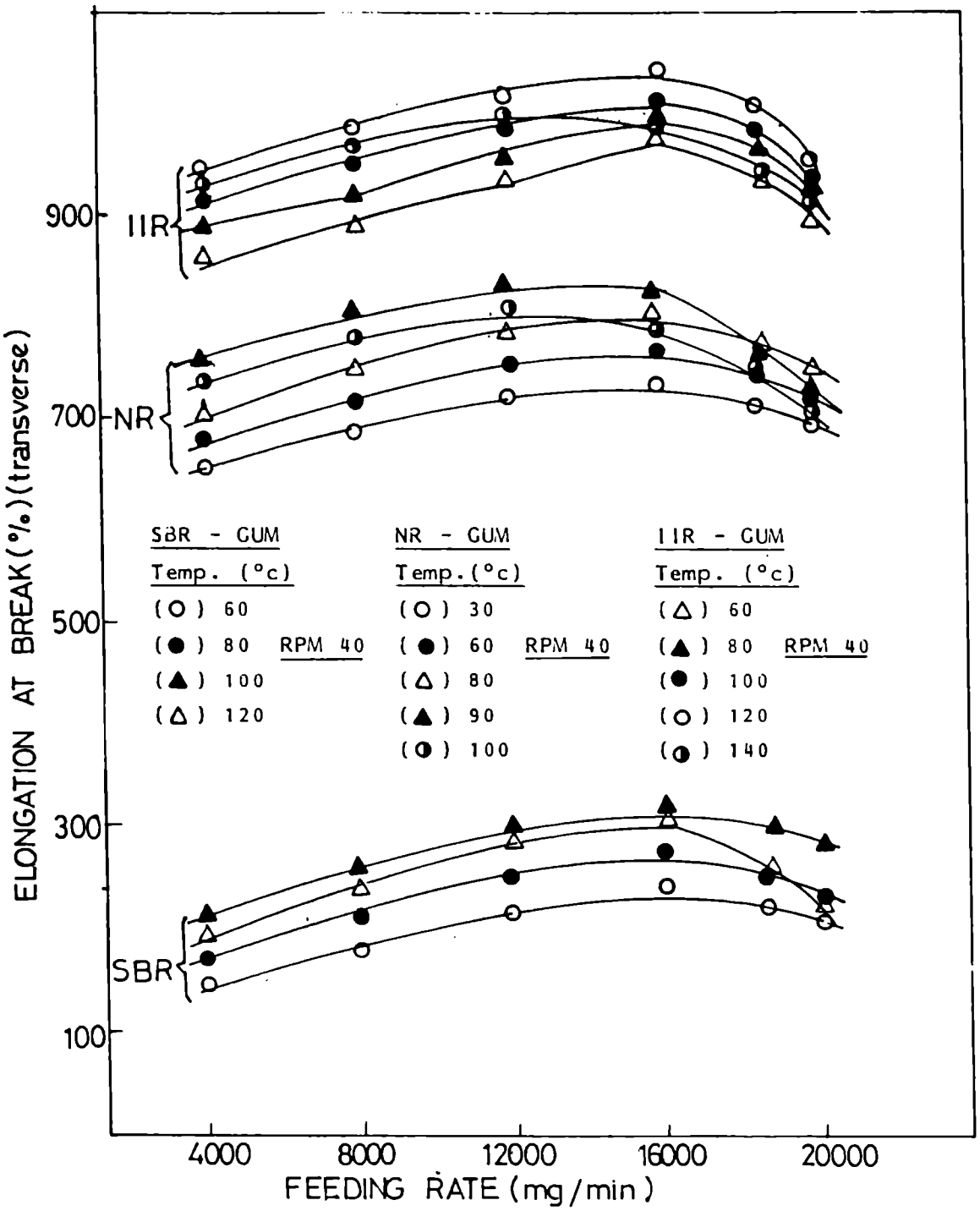


Fig.3.10: Variation of elongation at break of gum NR, SBR and IIR vulcanizates with feeding rate at different temperatures in the transverse direction.

at a fixed rpm in the milling/extrusion and transverse directions respectively. The behavior is more or less similar to those of the variations of the tensile strength.

3.3.2.2 Tear strength

Figure 3.11 shows the effect of feeding rate on the tear strength of the NR, SBR and IIR gum vulcanizates. It is found that the tear strength gradually increases with feeding rate and reaches a maximum value in the starve fed region (just below the flood feeding point) and thereafter decreases. This further confirms that there is a particular feeding rate in the starve fed region which result in maximum technical properties. The feeding rate is found to influence the tear strength of NR and IIR vulcanizates more pronouncely than that of SBR.

3.3.2.3 Hardness and compression set

Figure 3.12 shows the variation of hardness of NR, SBR and IIR gum vulcanizates with feeding rate. It is found that hardness increases with feeding rate and reaches a maximum value at the starve fed region and thereafter decreases at the flood fed and force fed regions as in the case of other properties. The maximum in hardness is observed at the starve fed level, just below the flood feeding point.

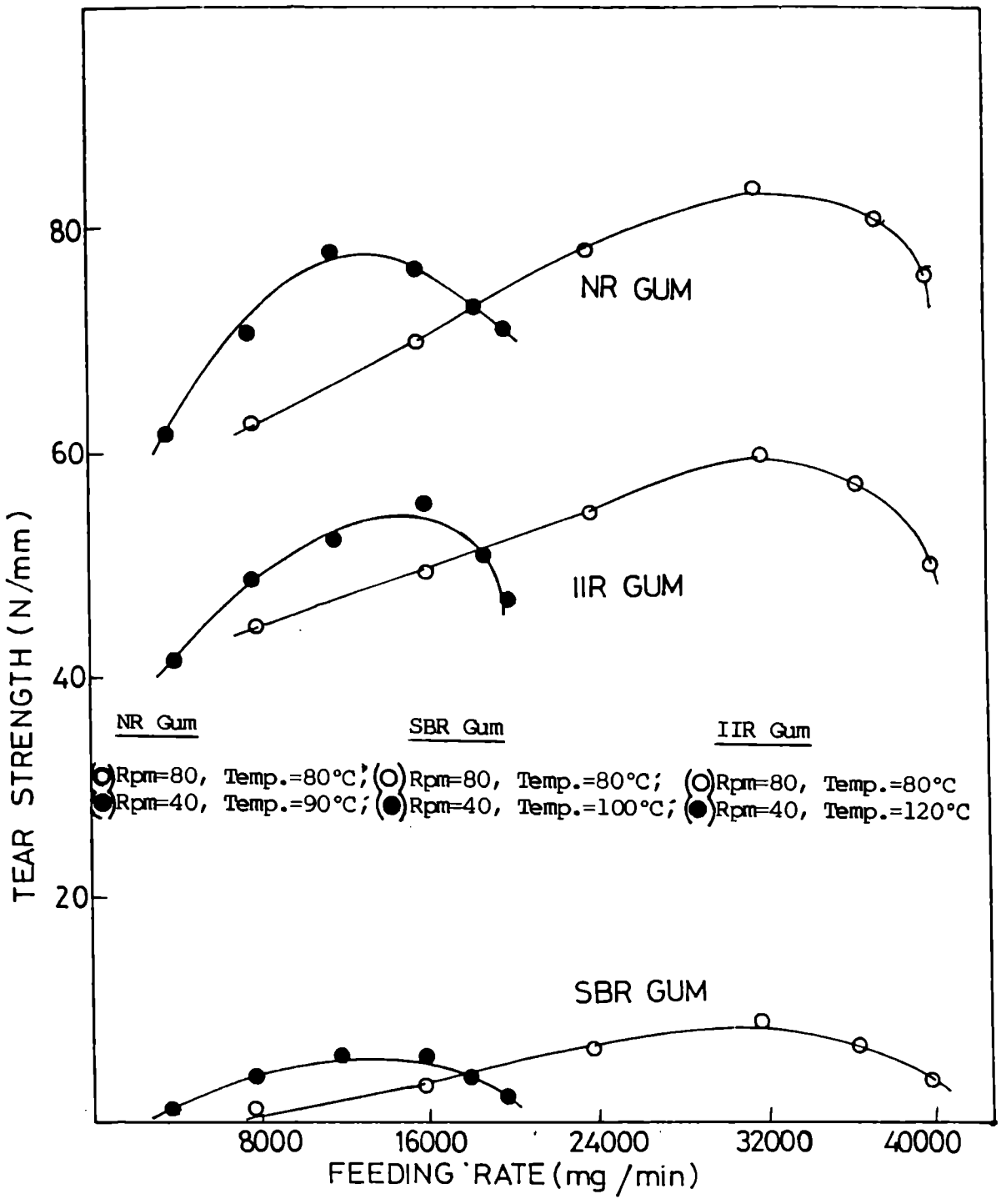


Fig.3.11: Variation of tear strength of gum NR, SBR and IIR vulcanizates with feeding rate at different rpms and temperatures.

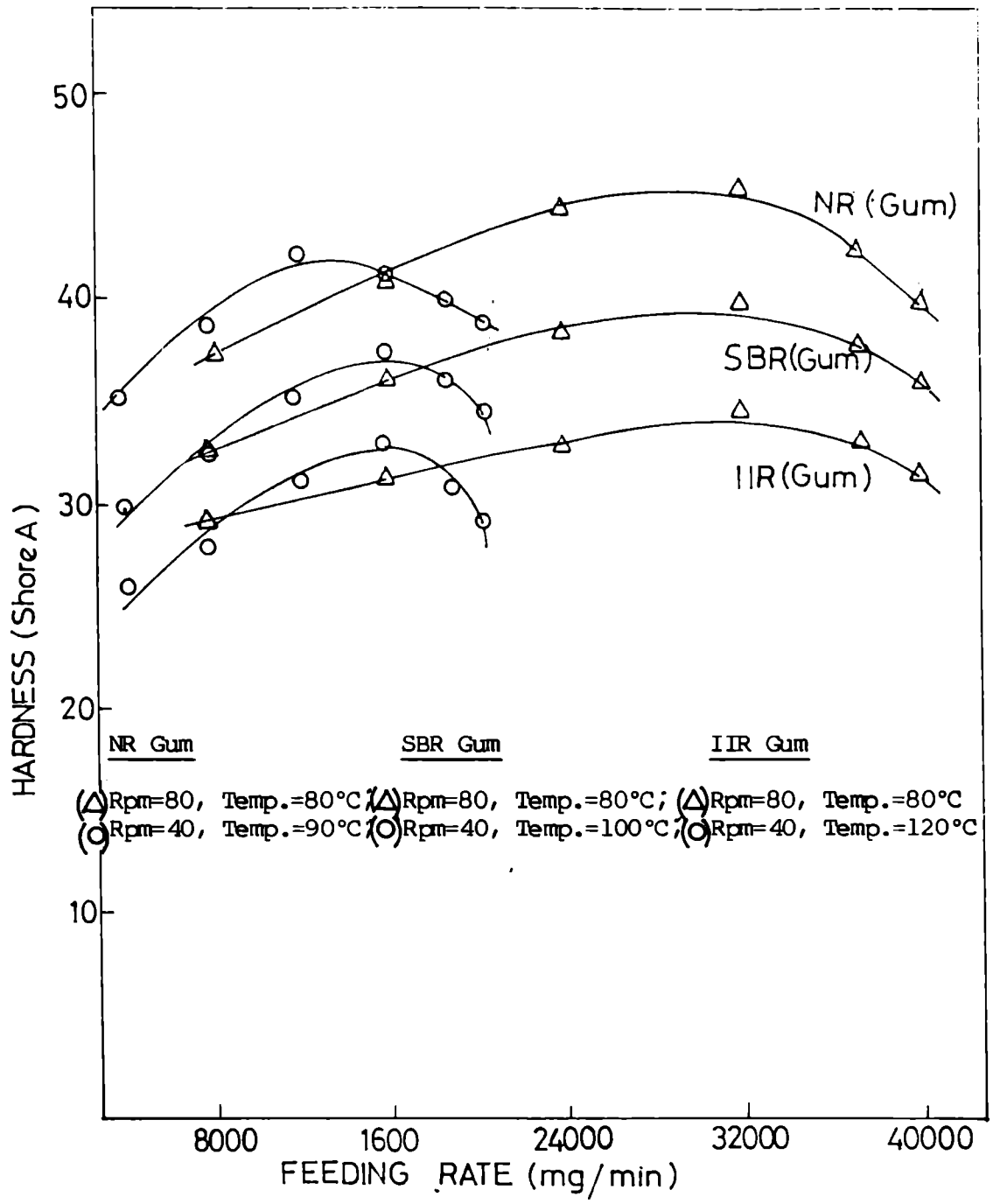


Fig.3.12: Variation of hardness of gum NR, SBR and IIR vulcanizates with feeding rate at different rpms and temperatures.

Figure 3.13 shows the variation of compression set with feeding rate of NR, SBR and IIR gum vulcanizates. The compression set decreases with feeding rate reaches a minimum value at the starve fed region and thereafter increases from the flood feeding point up to the force feeding point. This is probably due to the higher degree of crosslinking at the particular starve fed level which gave maximum physicals than at the flood fed, force fed levels and at higher levels of starving. This higher degree of crosslinking probably results from the uniform temperature distribution and shear history of the compounds in starved extrusion.[19]

3.3.3 Percentage of starvation and mechanical properties

Figure 3.14 shows the variation of tensile strength and elongation at break of NR extruded vulcanizates of compounds with the starvation level given as a percentage of the flood feeding at different rpms at a constant temperature of 80°C. Zero percentage starvation represents the flood feeding point. It is found that when the rpm increases the percentage of starvation at which maximum properties are observed decreases. In the case of NR, maximum properties are observed at percentage starvations of 14, 10, 9 and 8 respectively at rpms of 20, 40, 60 and 80 at a constant temperature 80°C.

Figure 3.15 shows the variation of tensile strength and elongation at break of NR vulcanizates of extruded compounds with percentage of

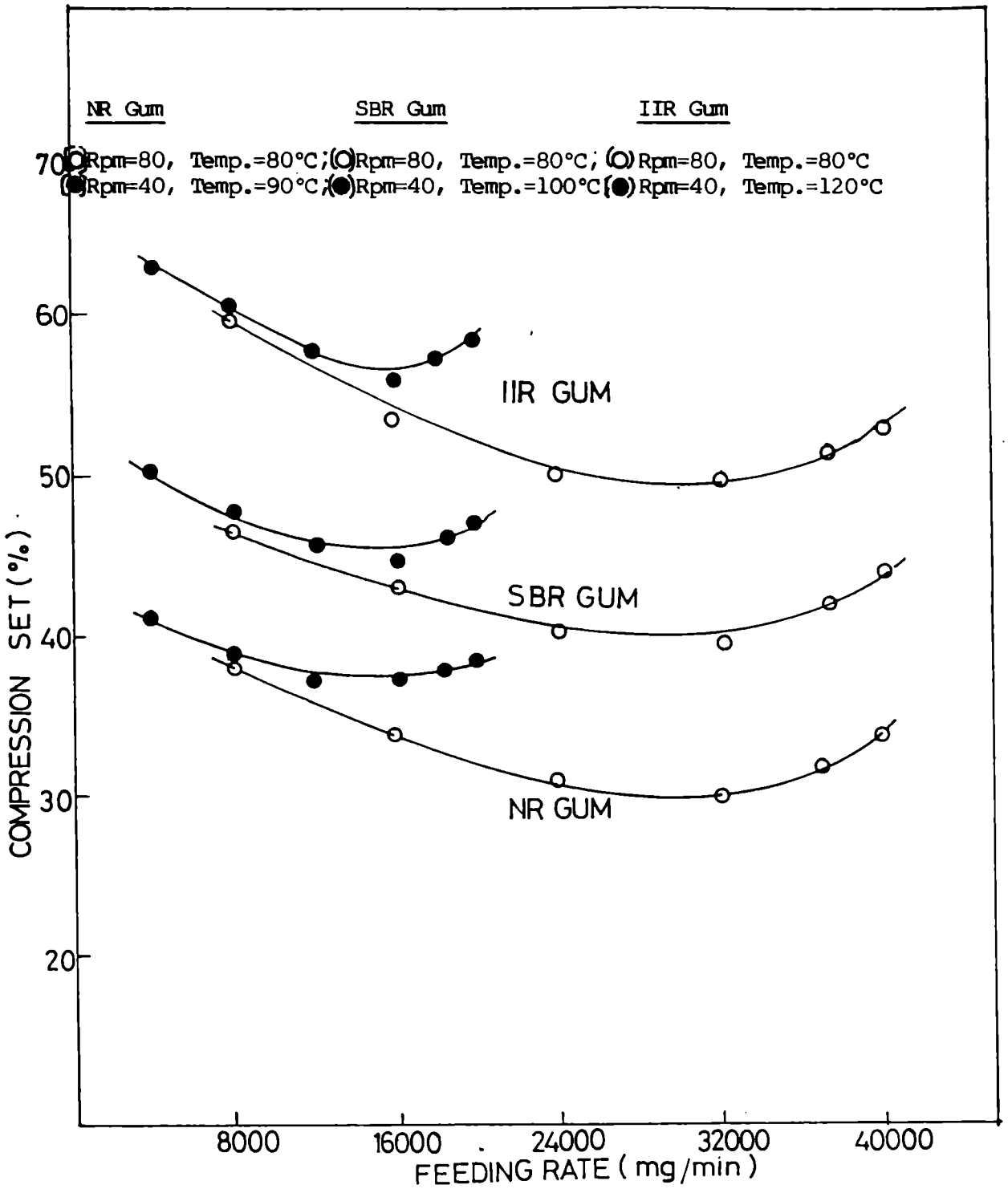


Fig.3.13: Variation of compression set of gum NR, SBR and IIR vulcanizates with feeding rate at different rpms and temperature.

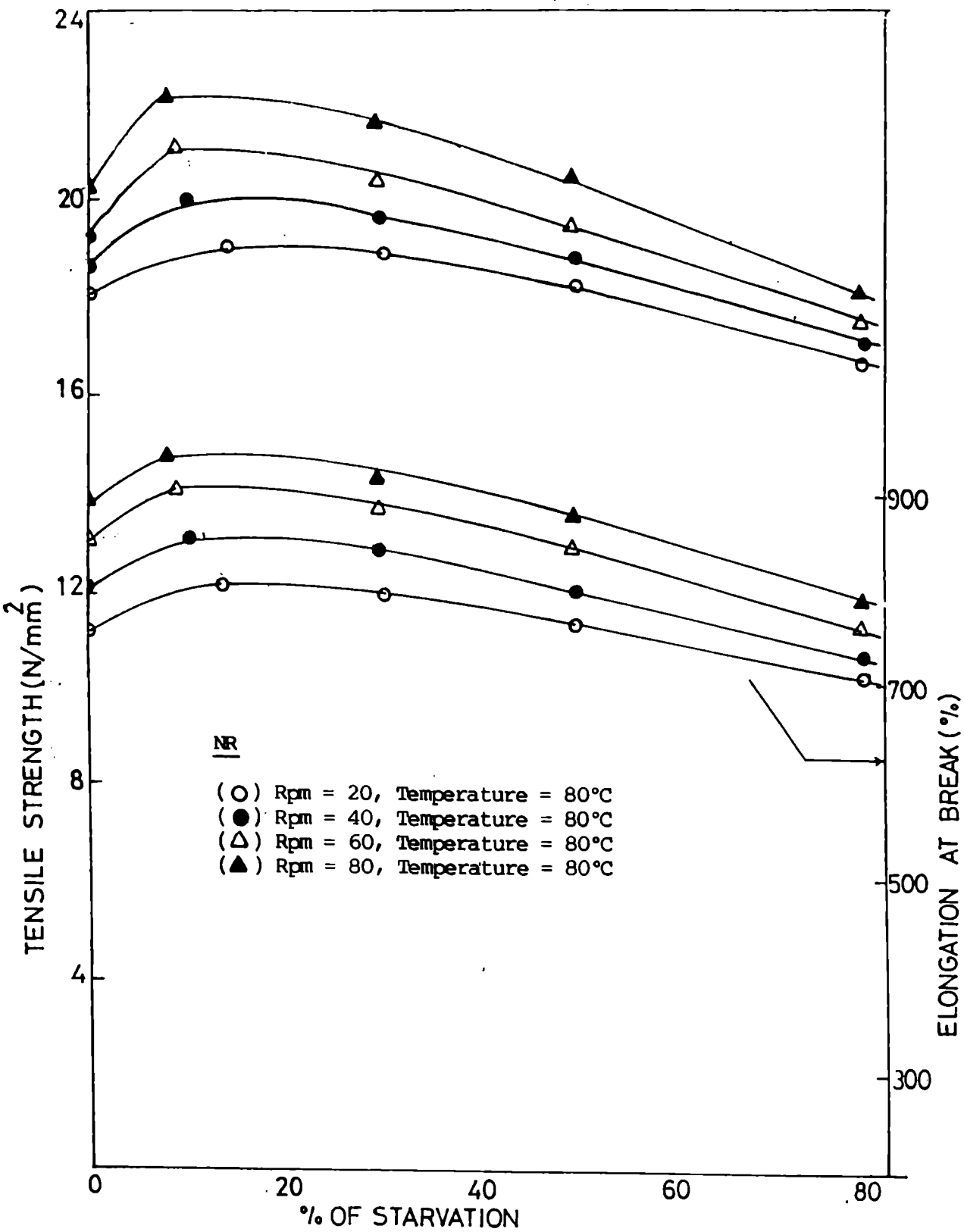


Fig.3.14: Variation of tensile strength and elongation at break of gum NR vulcanizates with percentage starvation at different rpms.

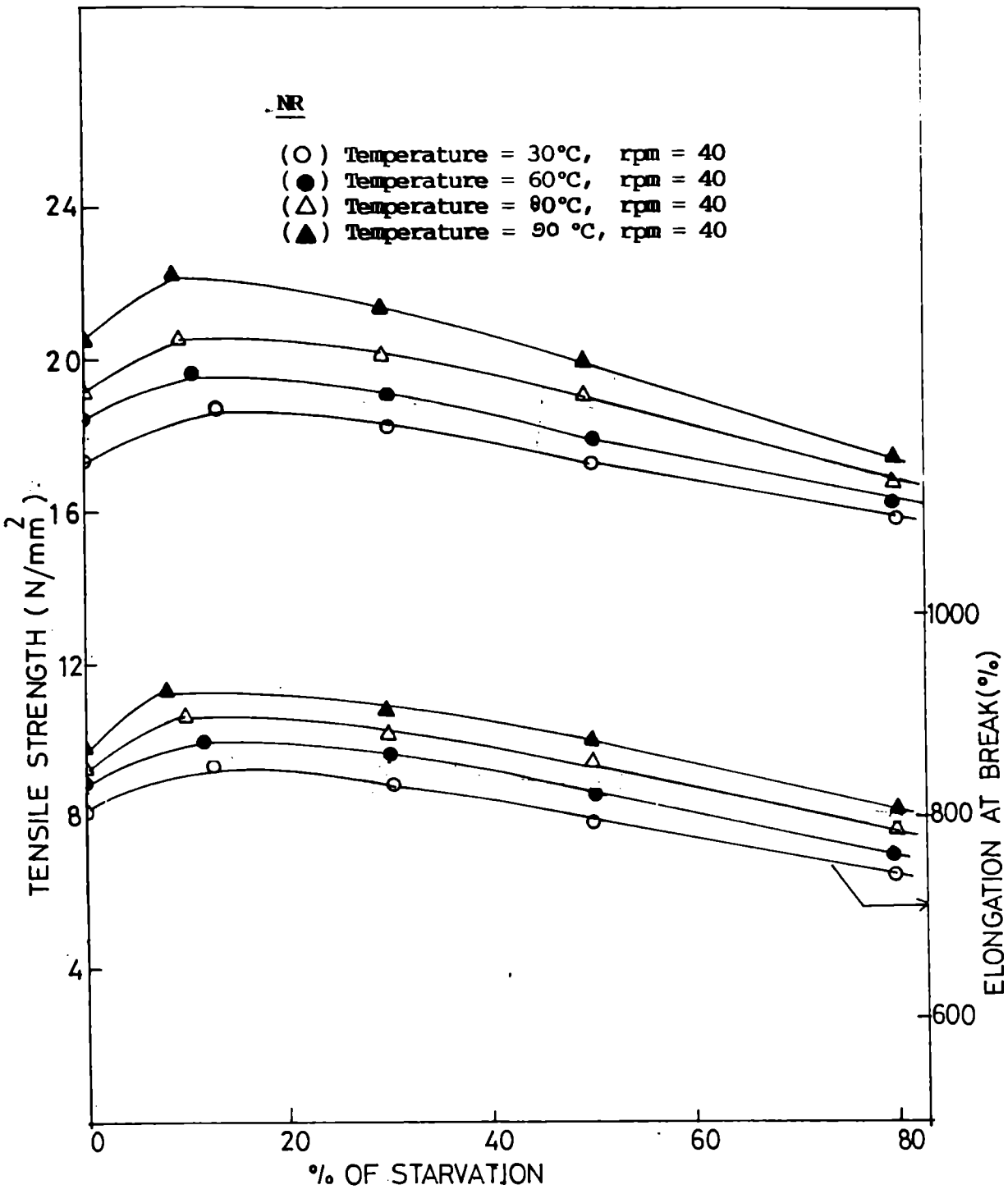


Fig.3.15: Variation of tensile strength and elongation at break of gum NR vulcanizates with percentage starvation at different temperatures.

starvation at different temperatures and at a fixed rpm of 40. It is found that the percentage of starvation at which maximum tensile properties are observed decreases with increase of temperature. Maximum properties are observed at percentage starvations of 15, 12, 10 and 9 respectively at temperatures of 30°C, 60°C, 80°C and 90°C at a fixed rpm of 40.

Figure 3.16 shows the variation of tensile properties of vulcanizates of SBR extruded compounds with percentage of starvation at different rpms and at a fixed temperature of 80°C. The percentage of starvation at which maximum properties are observed are 13, 11, 10 and 8 respectively at rpms of 20, 40, 60 and 80 at a constant temperature of 80°C.

Figure 3.17 shows the variation of tensile properties of SBR vulcanizates of extruded compounds with percentage of starvation at different temperatures and at a fixed rpm of 40. Maximum properties are obtained at percentage starvations of 12, 11 and 10 respectively at temperatures of 60°C, 80°C and 100°C.

Figure 3.18 represents the effect of percentage of starvation on the tensile properties of vulcanizates of IIR extruded compounds at different rpms and at a constant temperature of 80°C. The maximum properties are observed at percentage starvations of 13, 12.5, 12 and 11 respectively at rpms of 20, 40, 60 and 80. Figure 3.19 shows the effect of percentage of

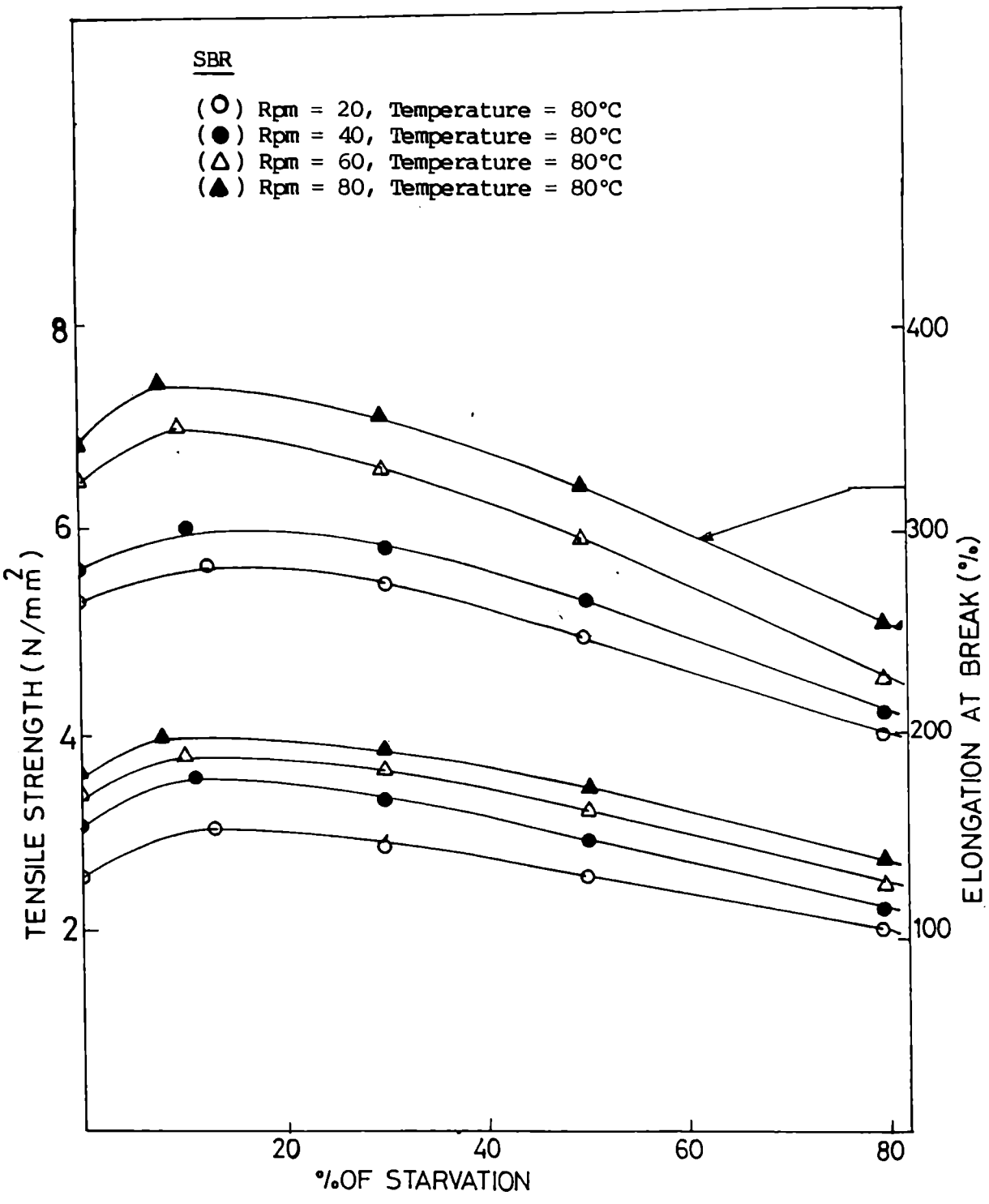


Fig.3.16: Variation of tensile strength and elongation at break of gum SBR vulcanizates with percentage starvation at different rpms.

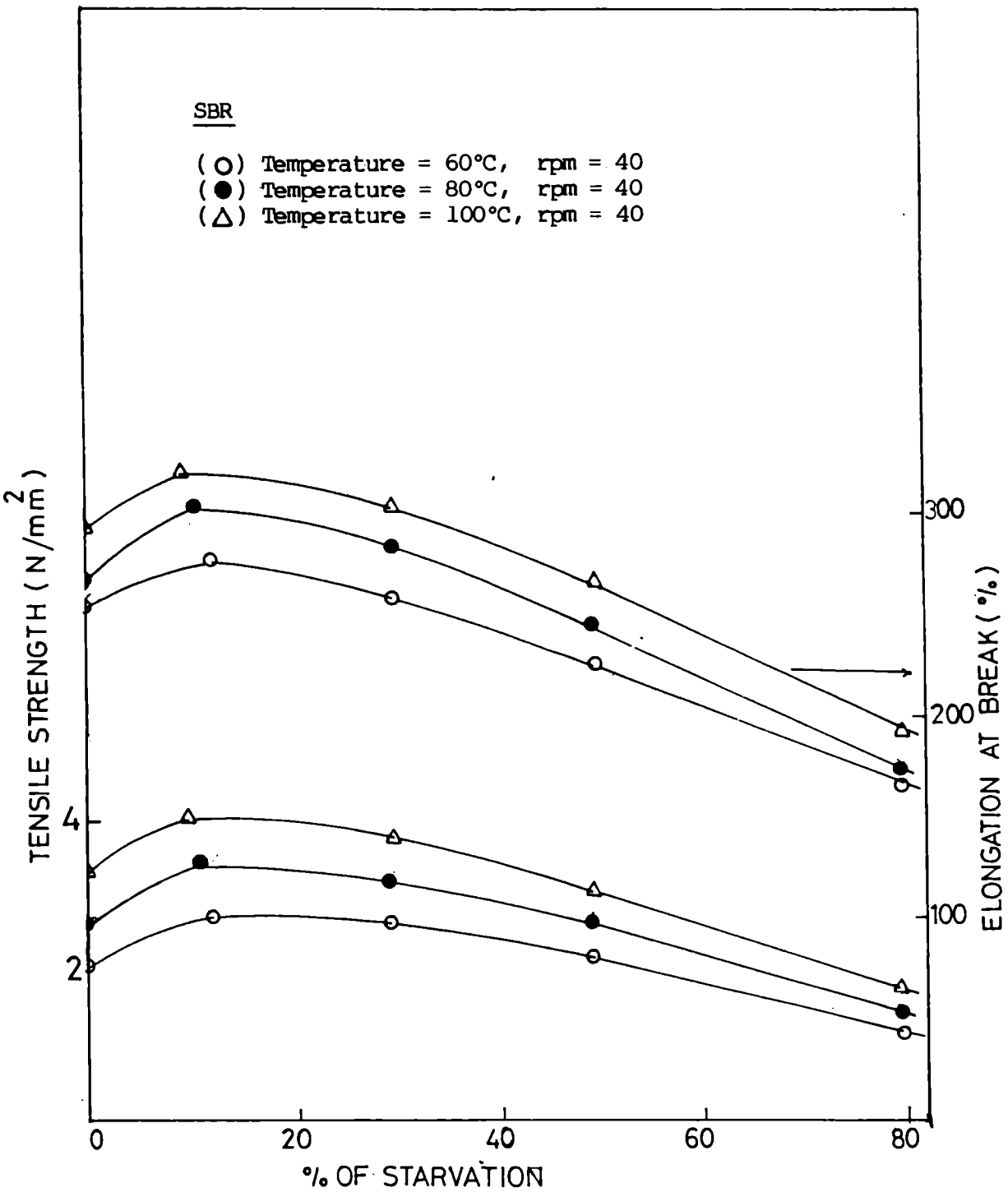


Fig.3.17: Variation of tensile strength and elongation at break of gum SBR vulcanizates with percentage starvation at different temperatures.

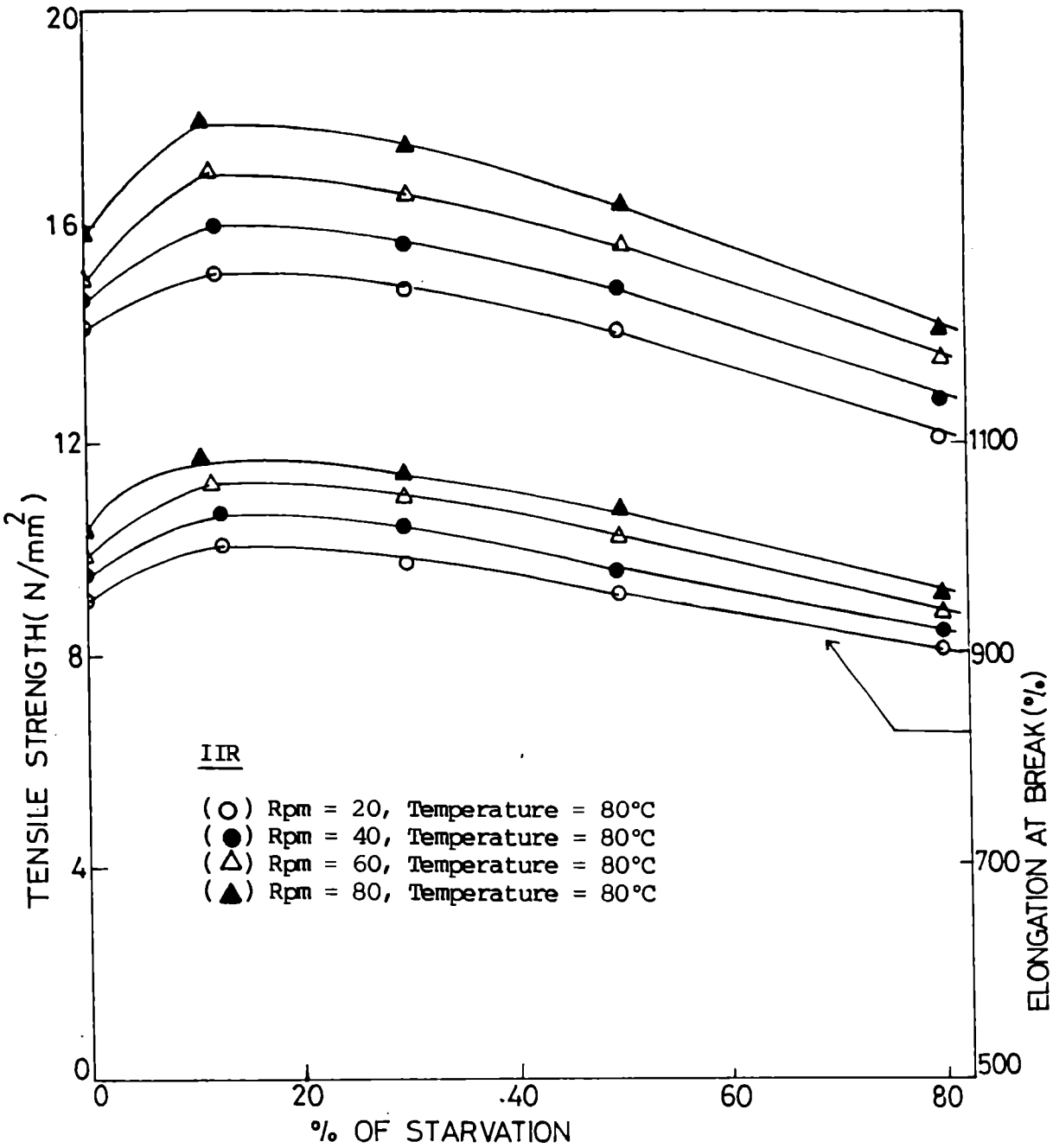


Fig.3.18: Variation of tensile strength and elongation at break of gum IIR vulcanizates with percentage starvation at different rpms.

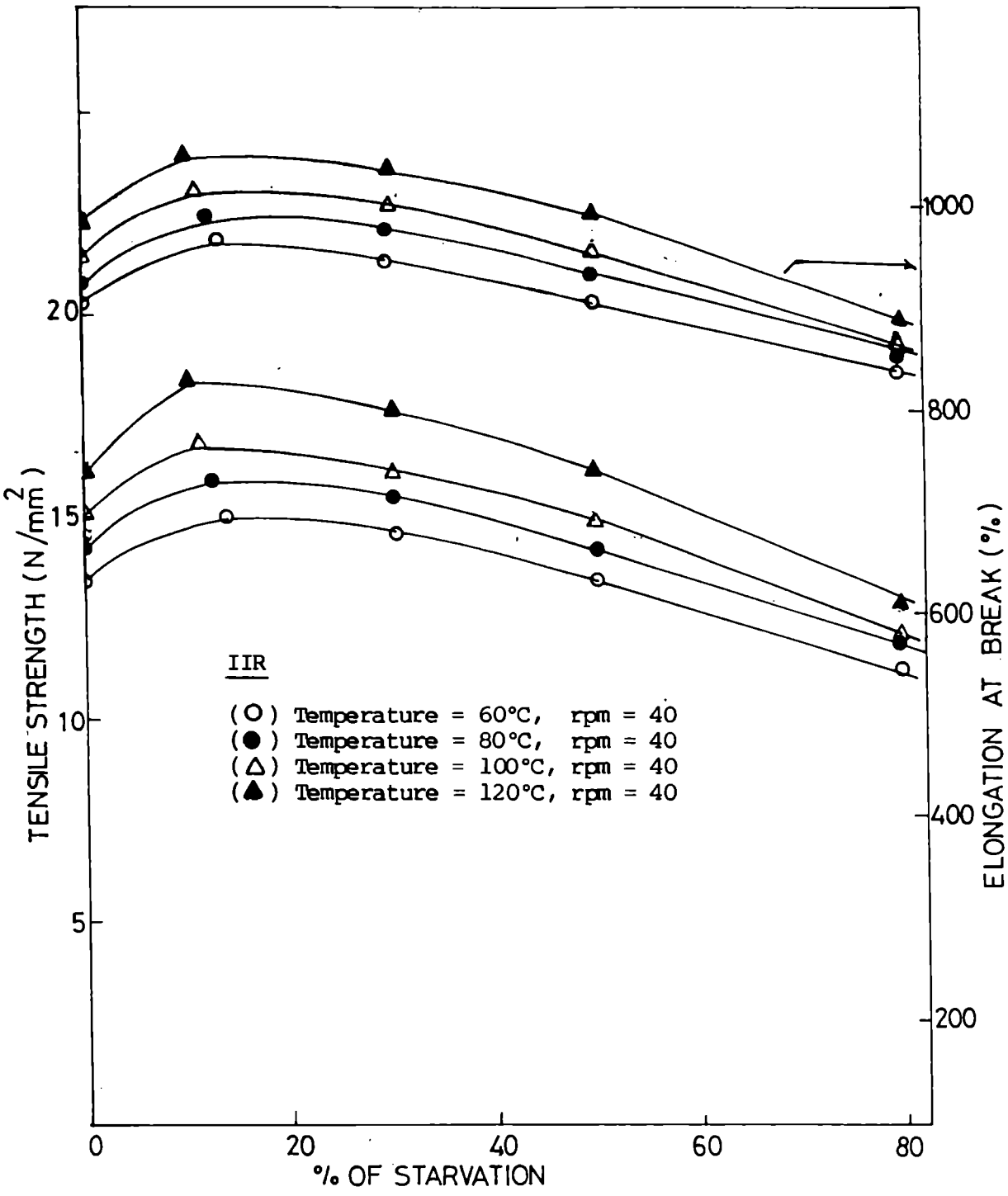


Fig.3.19: Variation of tensile strength and elongation at break of gum IIR vulcanizates with percentage starvation at different temperatures.

starvation on the tensile properties of IIR vulcanizates at different temperatures and at an rpm of 40. It is noticed that the percentage starvation which results in maximum properties are 14, 12.5, 11 and 10 respectively at temperatures of 60°C, 80°C, 100°C and 120°C.

The variation of other physical properties like tear strength, hardness and compression set with the percentage starvation are shown in Table 3.3a and 3.3b. Generally it may be concluded that the maximum properties of extrudates are observed at a low percentage of starvation.

3.3.4 Extrusion variables

Tables 3.4, 3.5 and 3.6 show the fluctuations of main extrusion variables viz., die temperature and flow rate in the extrusion of NR, SBR and IIR gum compounds respectively. At flood feeding (zero starvation), force feeding and at the higher levels of starvation the fluctuations in temperature and flow rate are appreciable. But at lower levels of starvation (mainly at 10% starvation) the fluctuations are relatively low. The quality of the extrudates depends substantially on the fluctuations of these extrusion variables.[27-29] The variation in the extrusion variables is in conformation with the observation that the die pressure fluctuations get reduced at low levels of starvation.[10]

Table 3.3a: Variation of physical properties of NR, SBR and IIR gum vulcanizates with percentage of starvation

% Starvation	NR Extruded at rpm 40 Temp. 90°C			SBR Extruded at rpm 40; Temp. 100°C			IIR Extruded at rpm 40; Temp. 120°C		
	Tear strength (N/mm)	Hardness (Shore A)	Compress-ion set (%)	Tear strength (N/mm)	Hardness (Shore A)	Compress-ion set (%)	Tear strength (N/mm)	Hardness (Shore A)	Compress-ion set (%)
80	61.24	32	38.71	1.51	30	46.81	40.95	25	49.81
50	65.02	36	36.23	1.70	32	44.11	45.88	27	47.72
30	70.34	39	34.01	2.51	35	42.15	52.30	29	45.51
10	76.31	43	32.22	3.22	38	40.08	57.99	32	44.02
0 (Flood feeding)	71.02	40	35.78	2.60	34	43.51	53.24	28	46.95
Force feeding	63.15	37	37.19	2.01	32	45.86	43.68	26	48.75

Table 3.3b: Variation of physical properties of NR, SBR and IIR gum vulcanizates with percentage of starvation

% Starvation	NR Extruded at rpm 80 Temp. 80°C			SBR Extruded at rpm 80; Temp. 80°C			IIR Extruded at rpm 80; Temp. 80°C		
	Tear strength (N/mm)	Hardness (Shore A)	Compress-ion set (%)	Tear strength (N/mm)	Hardness (Shore A)	Compress-ion set (%)	Tear strength (N/mm)	Hardness (Shore A)	Compress-ion set (%)
80	62.34	36	35.88	1.58	33	43.89	44.81	27	47.41
50	68.81	39	33.94	1.89	35	41.64	48.15	29	45.80
30	73.45	43	30.25	3.06	38	39.06	52.90	31	43.51
10	81.89	46	28.01	4.12	41	37.15	58.98	35	41.89
0 (Flood feeding)	75.08	43	32.75	3.28	37	40.95	53.46	32	43.94
Force feeding	66.46	40	36.81	2.51	34	42.81	45.78	30	44.88

Table 3.4: Fluctuations of temperature and flow rate in the extrusion of NR gum compounds at 1 min. intervals

Rpm	% Starvation	Temperature (°C)		Flow rate (mg/min)
		Set	Actual	
40	80	90	87	2990
			89	3895
			92	5001
			91	4100
			90	4011
40	50	90	88	8002
			90	8645
			91	9315
			92	10711
			91	9931
40	30	90	88	12990
			90	13801
			91	14403
			90	14000
			89	13040
40	10	90	89	16500
			89	16945
			90	17400
			89	17001
			90	17945
40	0 (Flood feeding)	90	88	18400
			89	19810
			88	19515
			90	20020
			88	18712
40	Force feeding	90	87	20345
			90	22167
			88	21190
			92	23005
			90	22850

Table 3.5: Fluctuations of temperature and flow rate in the extrusion of SBR gum compounds at 1 min. intervals

Rpm	% starvation	Temperature (°C)		Flow rate (mg/min)
		Set	Actual	
80	80	80	83	8001
			80	6840
			79	6712
			82	7520
			79	5995
80	50	80	82	17905
			80	16800
			81	17545
			79	16340
			78	15451
80	30	80	82	24950
			80	23855
			81	24225
			80	23800
			79	23000
80	10	80	79	29800
			79	30250
			79	30650
			80	30789
			80	30900
80	0 (Flood feeding)	80	80	34040
			82	35840
			80	34008
			82	35102
			79	33525
80	Force feeding	80	84	40000
			83	38800
			78	36740
			84	39545
			80	37625

Table 3.6: Fluctuations of temperature and flow rate in the extrusion of gum IIR compounds at 1 min. intervals

Rpm	% starvation	Temperature (°C)		Flow rate (mg/min)
		Set	Actual	
40	80	120	123	5110
			122	4310
			118	3014
			121	4012
			121	3750
40	50	120	122	10512
			120	9054
			122	9584
			118	7800
			120	9211
40	30	120	122	13200
			120	12814
			119	12400
			120	13300
			118	11812
40	10	120	121	17301
			121	16800
			120	16405
			120	16101
			119	16005
40	0 (Flood feeding)	120	122	19750
			119	17200
			120	17500
			121	18840
			118	16895
40	Force feeding	120	123	21014
			120	18800
			118	18518
			121	19714
			122	20014

3.3.5 Ageing studies

The variation of tensile strength and elongation at break before and after ageing for the NR, SBR and IIR vulcanizates is shown in Figs. 3.20-3.21. It is found that maximum retention in properties is observed at a low level of starvation at which maximum properties are observed for NR, SBR and IIR vulcanizates. This further shows the thermal and shear uniformity of the compounds at a particular low level of starvation.

Tables 3.7, 3.8 and 3.9 represent tensile properties before and after ageing at various levels of feeding with percentage retention. Figures 3.22–3.24 represent the bar charts of the tensile properties of the extruded vulcanizates at an rpm of 80 and at a temperature of 80°C. In the case of NR vulcanizates there is a large decrease in properties after ageing compared to SBR and IIR vulcanizates obviously due to the conversion of higher percentage of polysulphidic linkages to di and monosulphidic linkages and the main chain breakdown.[30,31]. But in the case of SBR and IIR vulcanizates, since there is more resistance to the main chain breakdown, there is only a marginal decrease in properties after ageing.[32]

3.3.6 Thermogravimetric analysis

Figures 3.25–3.27 represent the TGA traces of starve fed, flood fed and force fed samples of NR vulcanizates respectively, while Figs. 3.28–3.30 the TGA traces of corresponding samples of SBR vulcanizates

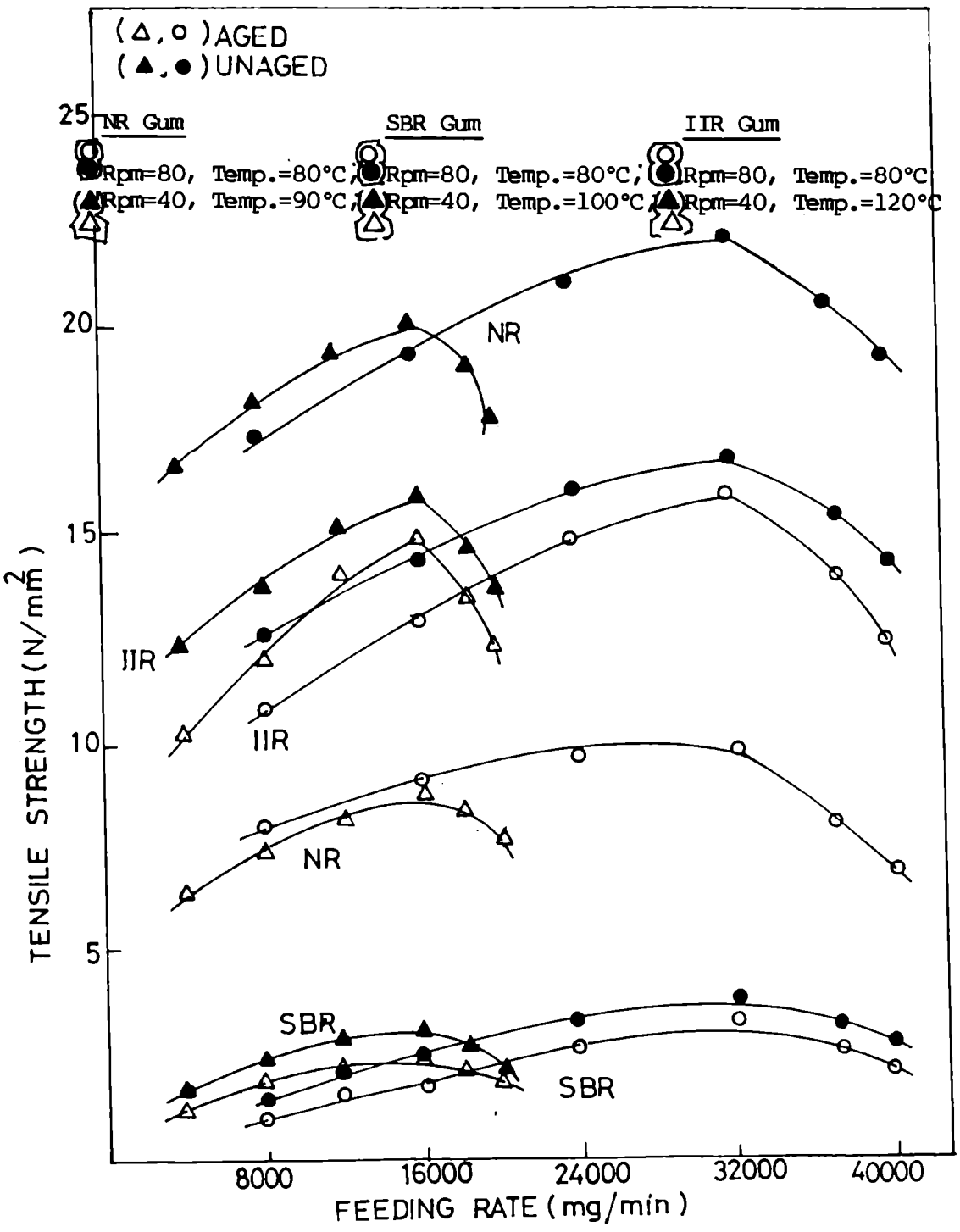


Fig.3.20: Variation of tensile strength of gum NR, SBR and IIR vulcanizates with feeding rate at different rpms and temperatures.

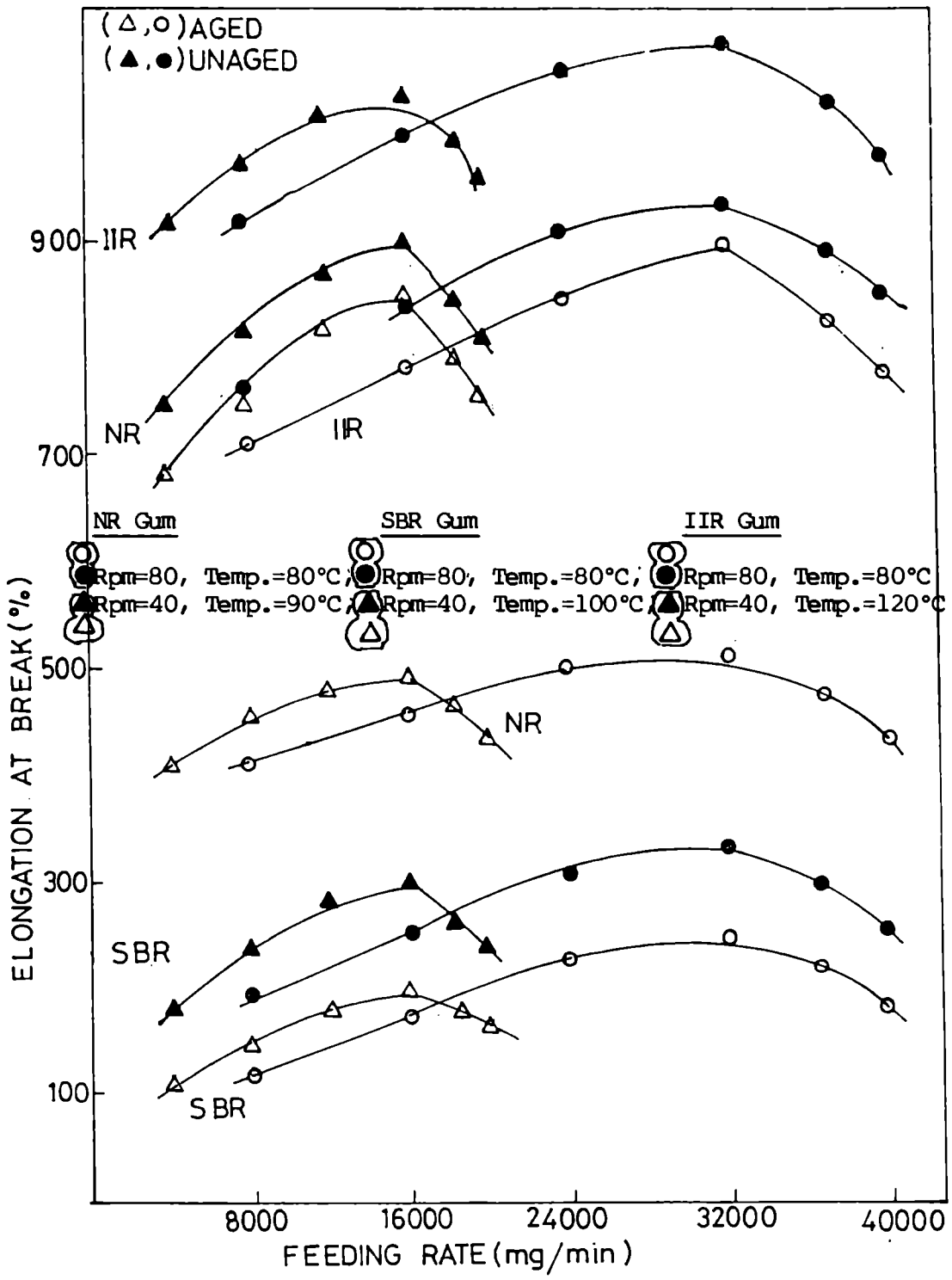


Fig.3.21: Variation of elongation at break of gum NR, SBR and IIR vulcanizates with feeding rate at different rpms and temperatures.

Table 3.7: Tensile properties of gum NR vulcanizates at different rpms and temperatures

	NR compounds extruded at rpm 40; Temperature 90°C						NR compounds extruded at rpm 80; Temperature 80°C					
	Tensile strength (MPa)			Elongation at break (%)			Tensile strength (MPa)			Elongation at break (%)		
% Starvation	Before ageing	After ageing	Retention %	Before ageing	After ageing	Retention %	Before ageing	After ageing	Retention %	Before ageing	After ageing	Retention %
80	17.0	6.5	38.2	750	405	54.0	17.5	8.0	45.7	760	415	54.6
50	18.2	7.5	41.2	820	455	55.5	19.5	9.0	46.2	845	470	55.6
30	19.5	8.2	42.1	875	490	56.0	21.0	9.9	47.1	910	520	57.1
10	20.0	9.0	45.0	900	515	57.2	22.2	10.9	49.1	928	540	58.2
0 (Flood feeding)	18.7	7.7	41.2	865	462	53.4	20.0	8.3	41.5	901	470	52.2
Force feeding	17.2	7.0	40.6	810	430	53.1	18.8	6.5	34.6	852	435	51.1

Table 3.8: Tensile properties of gum SBR vulcanizates at different rpms and temperatures

	SBR compounds extruded at rpm 40; Temperature 120°C						SBR compounds extruded at rpm 80; Temperature 80°C					
	Tensile strength (MPa)			Elongation at break (%)			Tensile strength (MPa)			Elongation at break (%)		
% Starvation	Before ageing	After ageing	Reten-tion %	Before ageing	After ageing	Retention %	Before ageing	After ageing	Reten-tion %	Before ageing	After ageing	Retention %
80	1.81	1.38	76.2	180	107	59.4	1.50	1.18	78.7	195	118	60.5
50	2.14	1.75	81.8	240	150	62.5	2.51	1.99	79.3	250	175	70.0
30	2.40	2.01	83.7	285	180	63.2	3.36	2.72	81.0	305	254	73.7
10	2.89	2.58	89.3	300	198	66.0	3.51	3.19	90.9	338	254	75.1
0 (Flood feeding)	2.48	2.00	80.6	270	174	64.4	3.01	2.35	78.1	295	210	71.2
Force feeding	2.01	1.55	77.1	245	155	63.3	2.68	2.05	76.5	263	180	68.4

Table 3.9: Tensile properties of gum IIR vulcanizates at different rpms and temperatures

% Starvation	IIR compounds extruded at rpm 40; Temperature 120°C						IIR compounds extruded at rpm 80; Temperature 80°C					
	Tensile strength (MPa)			Elongation at break (%)			Tensile strength (MPa)			Elongation at break (%)		
	Before ageing	After ageing	Retention %	Before ageing	After ageing	Retention %	Before ageing	After ageing	Retention %	Before ageing	After ageing	Retention %
80	12.30	10.25	83.3	910	695	76.4	12.60	11.12	88.3	924	712	77.1
50	13.75	12.12	88.1	960	756	78.8	14.70	13.21	89.7	993	778	78.3
30	15.27	14.01	91.7	1012	825	81.5	16.25	15.19	93.5	1060	854	80.6
10	16.25	15.43	95.00	1030	857	83.2	17.40	16.51	94.9	1081	905	83.7
0 (Flood feeding)	15.00	13.81	92.10	1001	764	76.3	16.10	13.59	84.4	1023	837	81.8
Force feeding	13.71	12.45	90.8	962	729	75.8	14.75	12.28	83.3	980	777	79.3

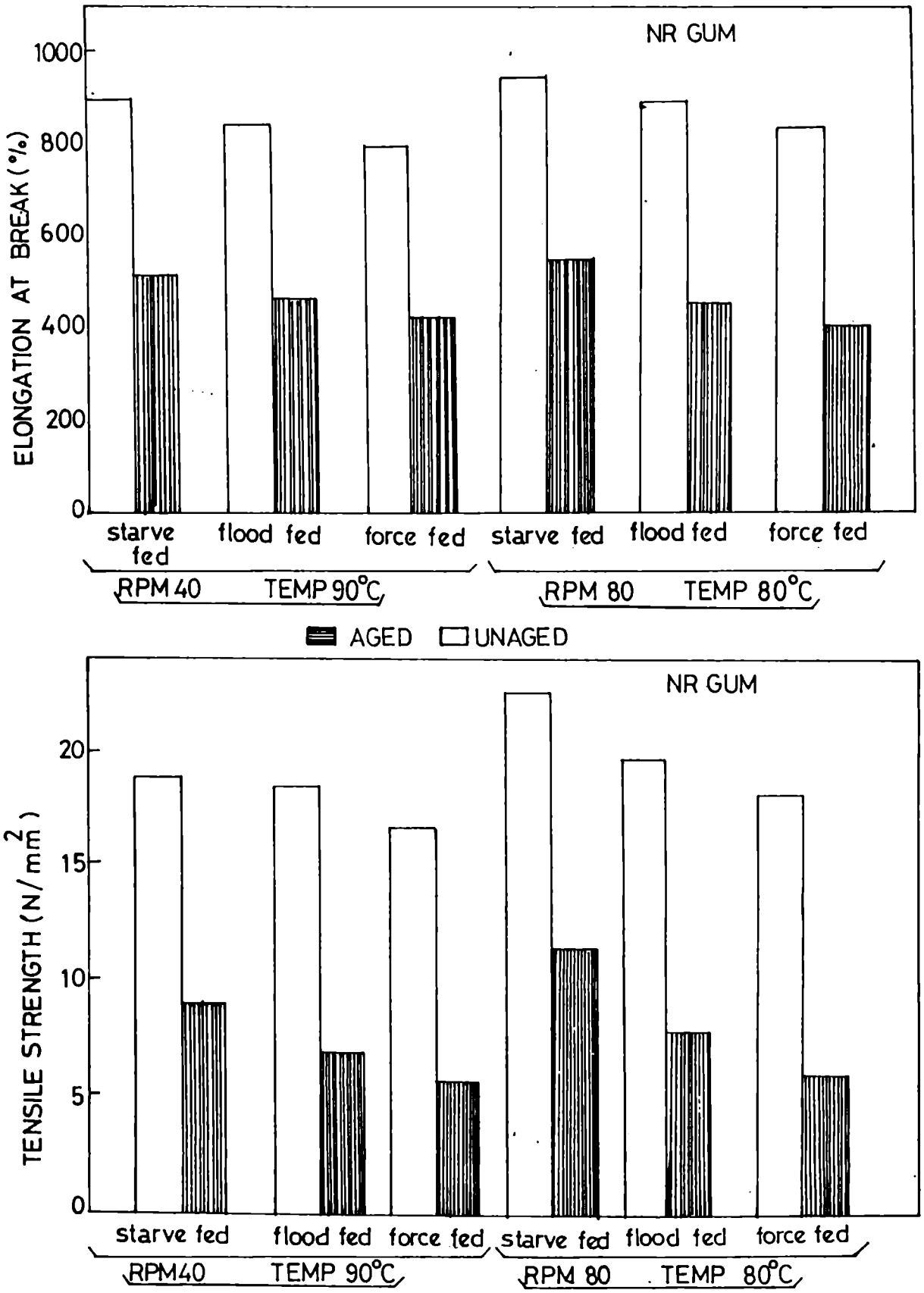
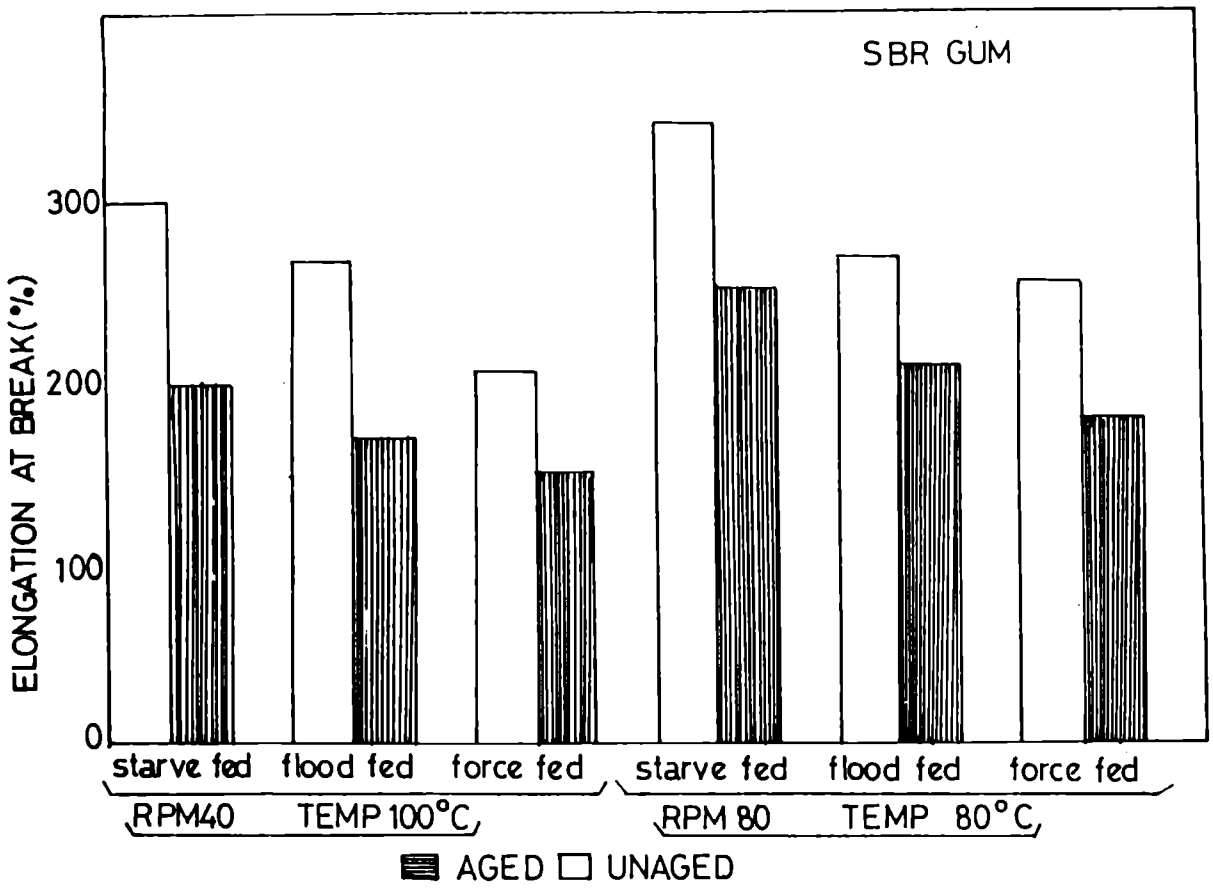


Fig.3.22: Variation of tensile strength and elongation at break of gum NR vulcanizates with different levels of feeding at different rpms and temperatures.



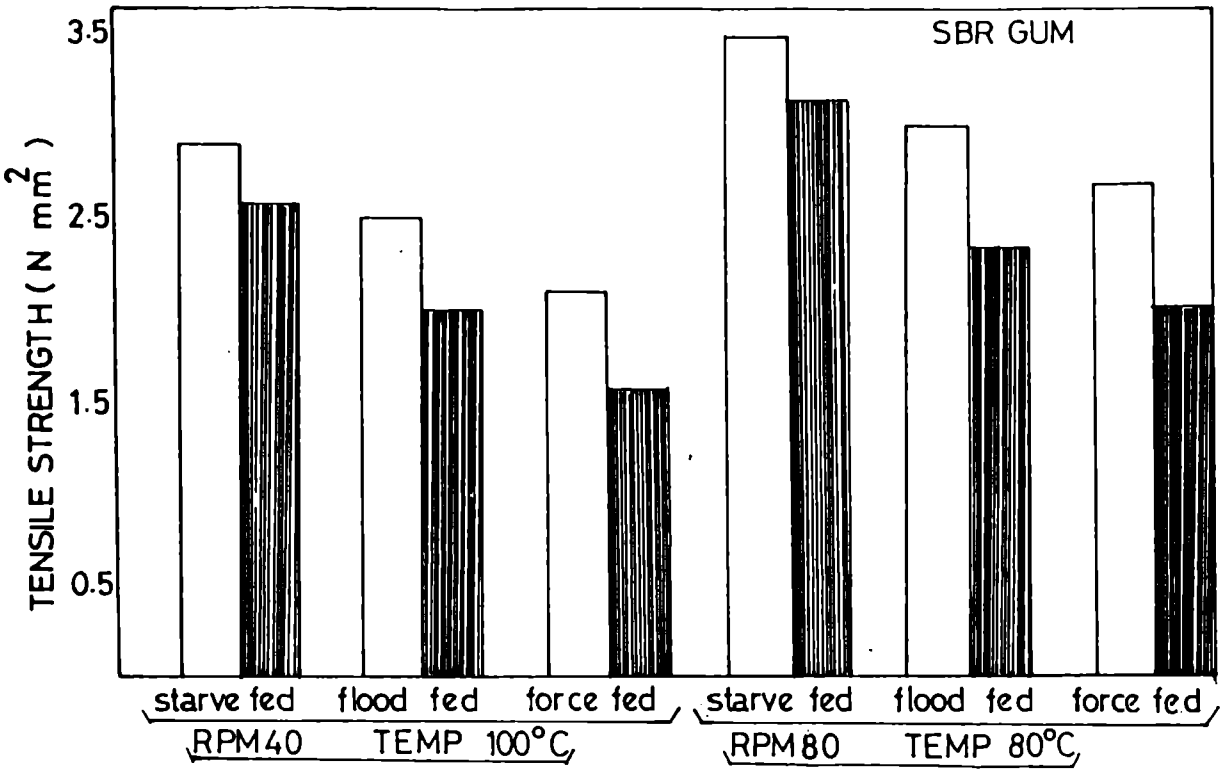


Fig.3.23: Variation of tensile strength and elongation at break of gum SBR vulcanizates with different levels of feeding at different rpms and temperatures.

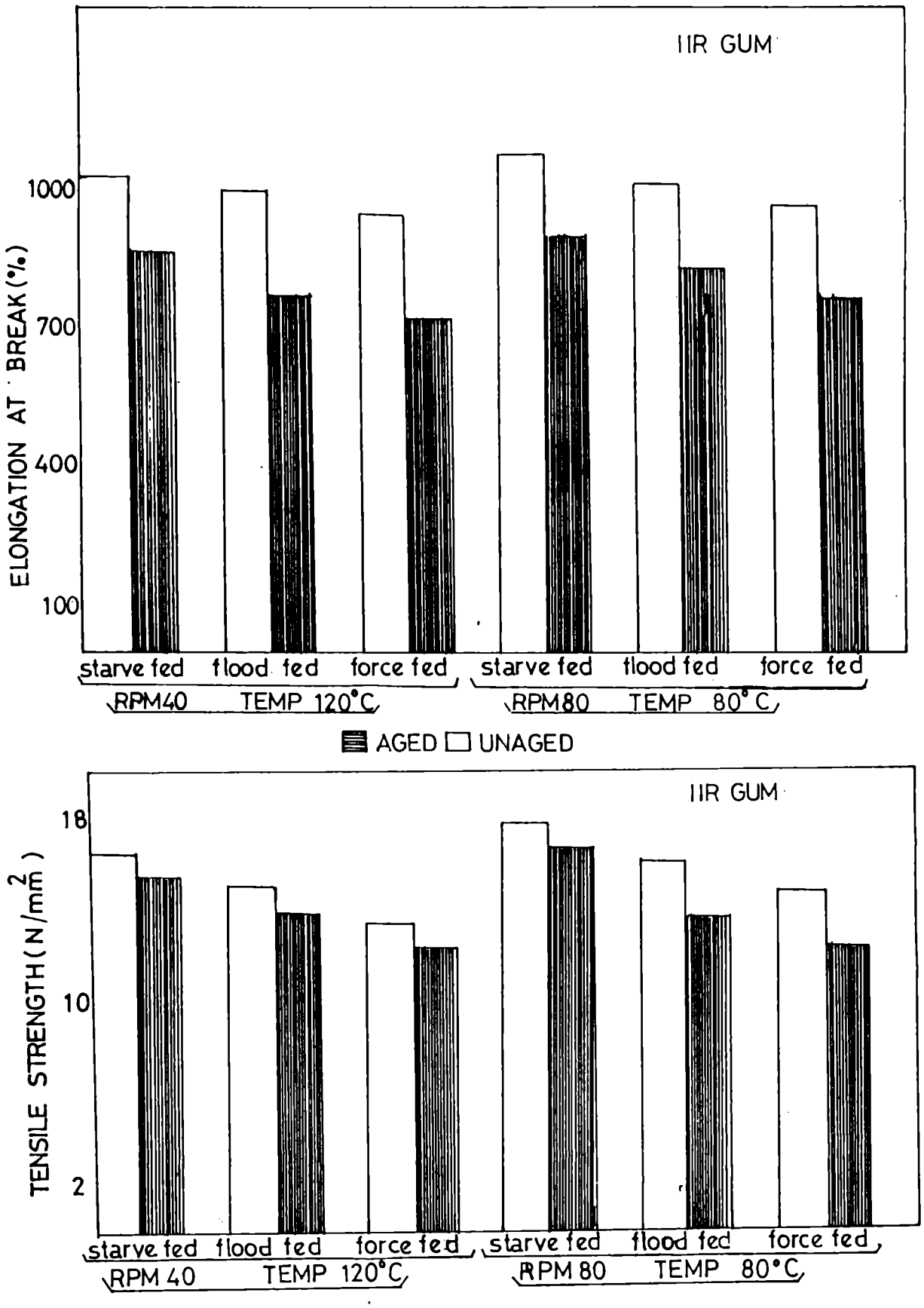


Fig.3.24: Variation of tensile strength and elongation at break of gum IIR vulcanizates with different levels of feeding at different rpms and temperatures.

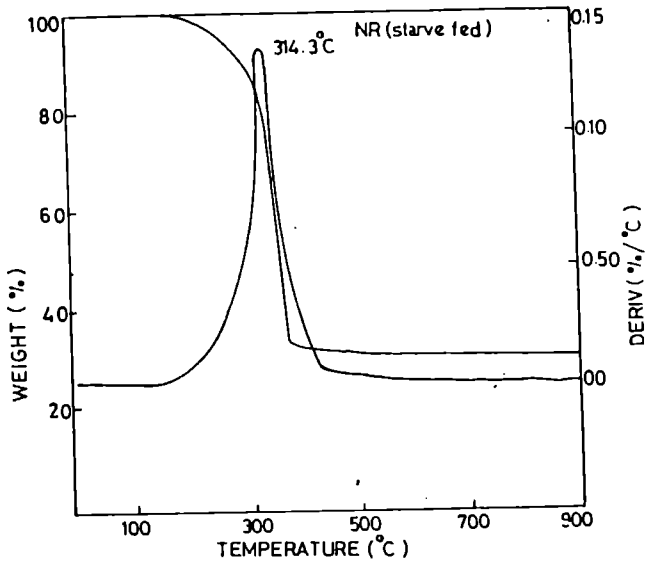


Fig.3.25
Starve fed

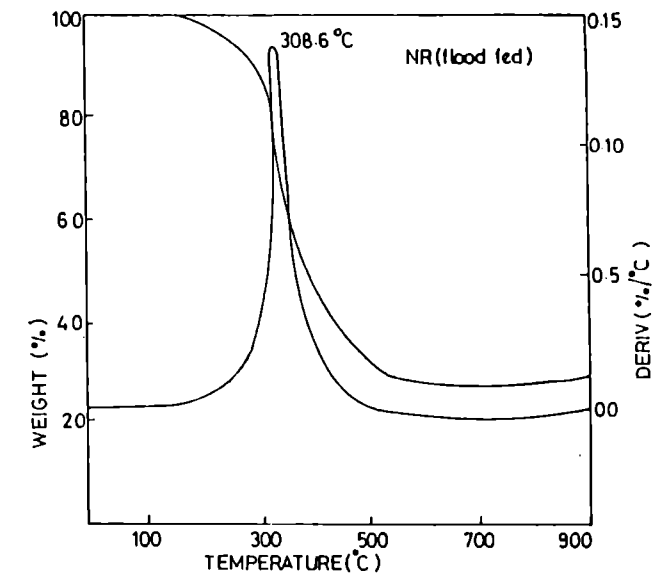


Fig. 3.26
Flood fed

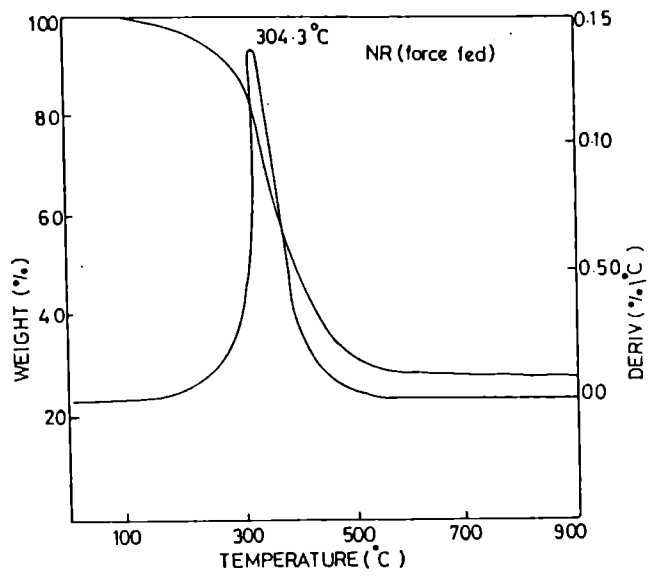


Fig.3.27
Force fed

TGA traces of gum vulcanizates of NR Compounds.

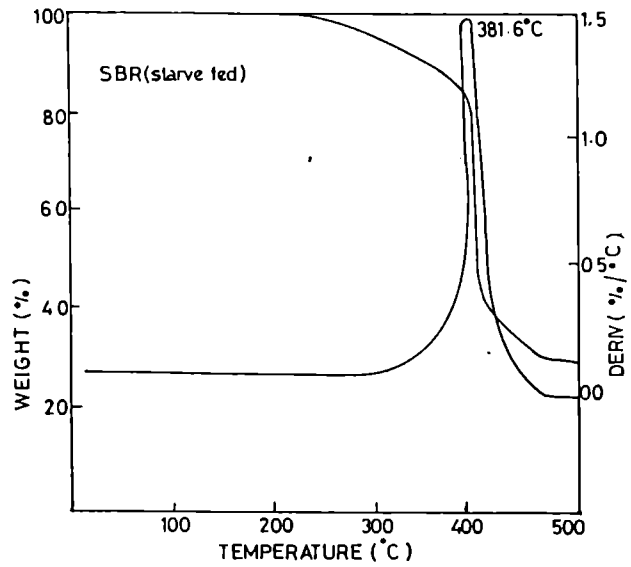


Fig.3.28
Starve fed

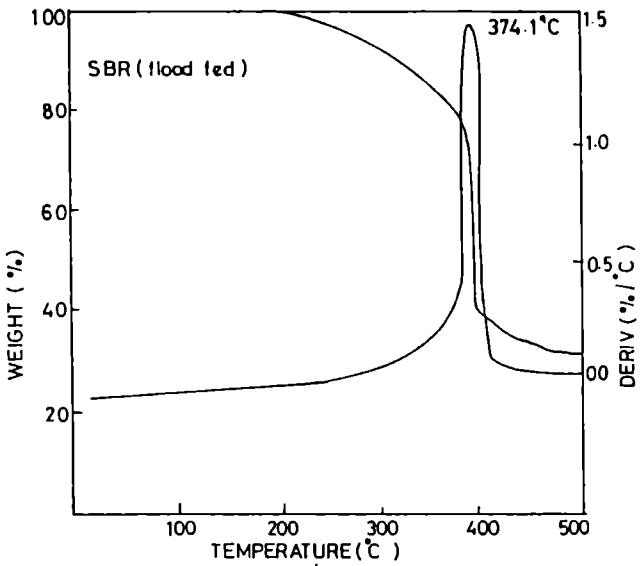


Fig.3.29
Flood fed

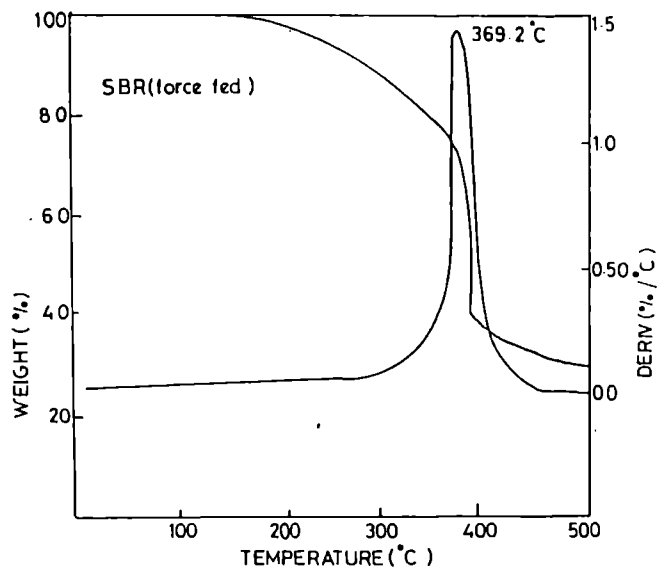


Fig.3.30
Force fed

TGA traces of gum vulcanizates of SBR compounds.

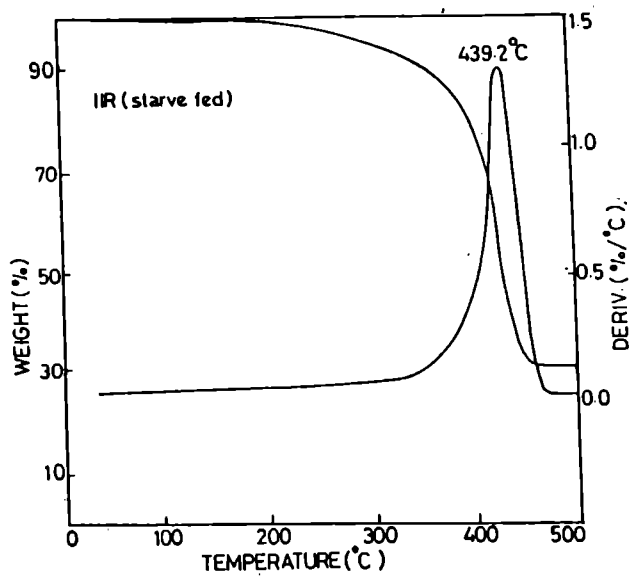


Fig.3.31
Starve fed

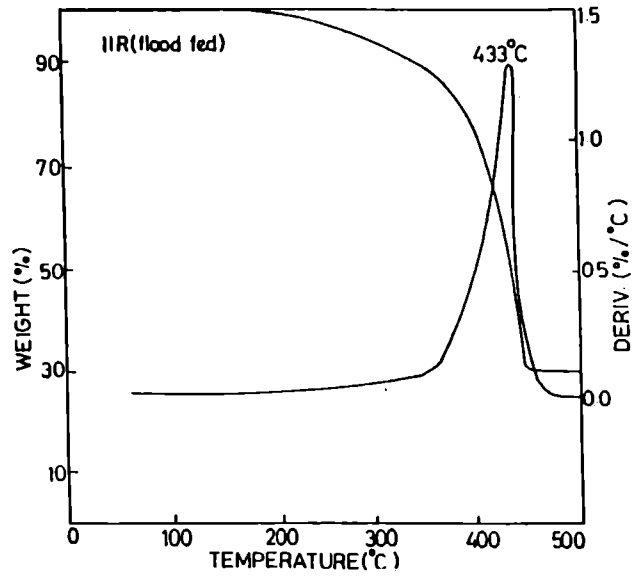


Fig.3.32
Flood fed

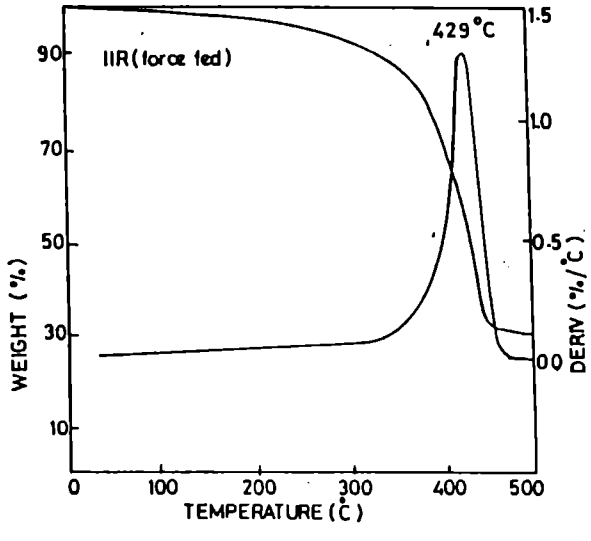


Fig.3.33
Force fed

TGA straces of gum vulcanizates of IIR compounds.

respectively and Figs. 3.31–3.33 the TGA traces of the corresponding samples of IIR vulcanizates respectively. It may be observed that the starve fed sample has higher transition temperature than the flood fed sample which in turn has higher transition temperature than the force fed sample. This shows that the starve fed compound (at a level of low starvation) is more thermally stable than the normally fed sample which in turn is more stable than the force fed sample. This behavior obviously results from the more uniform temperature and shear history to which the compound was subjected to under starved extrusion than the normal/forced extrusion.

3.3.7 Density and viscosity

Table 3.10 shows the variation in the density of a few sets of samples of gum vulcanizates of extruded NR, SBR and IIR. The densities of the vulcanizates decrease marginally with the degree of starving as expected. In the case of NR vulcanizates the density of the sample at the low level of starvation is more or less the same as that of the flood fed sample. But in the case of SBR and IIR vulcanizates the density of the sample at the low levels of starvation is only slightly less than that of the corresponding flood fed samples.

Table 3.10 also shows the variation in Brookfield viscosity of the solutions of a certain samples of extruded NR, SBR and IIR compounds. The

Table 3.10: Variation of density, Brookfield viscosity, swelling index, total crosslink density of gum NR, SBR and IIR vulcanizates with percentage of starvation

	Feeding rate (mg/min)	Percentage starvation	Density (g/cc)	Viscosity (centipoise)	Swelling index	Total crosslink density x 10^5 g mol/cm^3
NR extruded at 40 rpm and 80°C	3600	80	0.9175	201200	3.68	4.55
	9000	50	0.9182	202000	3.55	4.92
	12600	30	0.9188	202800	3.44	5.12
	16200	10	0.9192	203700	3.30	5.99
	18000	0 (Flood feeding)	0.9194	202500	3.62	4.65
	20000	Force feeding	0.9193	202300	3.74	4.42
SBR extruded at 80 rpm and 80°C	7200	80	0.9380	43600	3.51	5.08
	18000	50	0.9383	44400	3.32	5.46
	25200	30	0.9387	45200	2.96	5.68
	32400	10	0.9390	46400	2.41	6.21
	36000	0 (Flood feeding)	0.9394	44500	2.63	5.50
	40000	Force feeding	0.9391	44800	2.75	5.25
IIR extruded at 40 rpm and 120°C	3600	80	0.9263	18200	2.27	6.85
	9000	50	0.9266	18520	1.97	7.23
	12600	30	0.9271	18940	1.89	7.51
	16200	10	0.9276	19320	1.71	8.01
	18000	0 (Flood feeding)	0.9280	18600	1.94	7.12
	20000	Force feeding	0.9278	18350	2.02	6.99

viscosity increases with feeding rate, in the starved region reaches a maximum value and then decreases as in the case of the variation of physical properties. So it may be observed that the samples which give maximum physical properties show the highest value of viscosity. The viscosity values of the samples at flood fed and force fed levels are lower than those at the low level of starvation at which maximum properties were observed. This points towards the lower mechanical breakdown in the case of starve fed sample.[33-35]

3.3.8 Swelling index and crosslink density

Table 3.10 shows the variation in swelling index and crosslink density ($\frac{1}{2}M_c$) of the samples of NR, SBR and IIR gum vulcanizates. It may be noticed that the samples, which give maximum physical properties, show the least swelling index and maximum crosslink density.[36,37]

3.4 CONCLUSIONS

The study shows that the feeding rate in a single screw extrusion has a profound effect on the network structure of the rubber extrudates and the following conclusions can be drawn.

1. Starve feeding of NR, SBR and IIR compounds results in better mechanical properties of the vulcanizates at a particular low level of

starvation i.e. for a given screw there is an optimum feeding rate in the starved region which results in maximum physical properties.

2. This improvement in mechanical properties of NR, SBR and IIR is observed at different rpms of the screw.

3. The properties generally improve with temperature till the onset of thermal degradation.

4. The effect of feeding rate on the mechanical properties is more pronounced in NR vulcanizates rather than SBR and IIR vulcanizates.

5. The fluctuations of extrusion variables, like temperature and flow rate are minimum at the starvation levels at which maximum properties are observed.

REFERENCES

1. A.Schneiders, Plastverarbeiter 19, 797 (1968).
2. R.Brozoskowski, J.L.White, Int. Polym. Process, 2, 102 (1987).
3. R.Brozoskowski, K.Kubota, K.Chung, J.L.White, F.C.Weissert, N.Nakajima and K.Min. Int. Polym. Process, 1, 130 (1987).
4. K.Kubota, R.Brozoskowski, J.L.White, F.C.Weissert, N.Nakajima and K.Min. Rubb. Chem. Technol., 60, 924 (1987).
5. K.Ramamurthy and S.Lakshmanan, Inter. Plast. Eng. And Tech., 1, 59 (1994).
6. Russel J.Nichols and George A.Kruder, SPE Journal 20, 463 (1974).
7. P.H.Squires, SPE Journal, 14, 24 (1958).
8. B.H.Maddock, SPE—15th ANTEC, 5, 211 (1959).
9. J.P.Tordella, J. Appl. Polym. Sci., 7, 215 (1963).
10. D.P.Isherwood, R.N.Pieris and D.Valamonte, Plast. Rubb. Processing Appl., 4, 257-260 (1984).
11. D.M.Bigg, Polym. Plast. Technol. Eng., 23, 134 (1984).
12. R.S.Spencer, R.M.Wiley, J. Colloid. Sci., 6, 133, 1951.
13. G.Pinto and F.Tadmor, Polym. Eng. Sci., 10, 279 (1970).
14. D.M.Bigg and S.Middleman, Ind. Eng. Chem. Fundam., 13, 66 (1974).
15. R.Brozoskowski, J.L.White, F.C.Weissert, N.Nakajima and K.Min., Rubb. Chem. Technol., 59, 634 (1986).
16. G.Menges and J.P.Lehnen Kunststoff Technik, 9, 352 (1986).

17. B.Ellis, G.N.Welding, Techniques of Polymer Science, Soc. Chem. Ind., London, 46 (1964).

18. P.J.Flory, J. Rehner, J. Chem. Phys., 11, 512 (1943).

19. B.Saville, A.A.Watson, Rubber Chem. Technol., 40, 100 (1967).

20. R.T.Fenner, A.P.D.Cox and D.P.Isherwood, Polymer, 20(6), 733-736 (1979).

21. D.P.Isherwood, R.N.Pieris, J.Kassatly and D.Valamonte, "Some Experiments on Metered Starve Feeding in the Extrusion Process", ASME Design and Production Engineering Conferences, Washington, pp.135-44 (1982).

22. L.Erwin SPE ANTEC. Tech. Pap.24, 488 (1978).

23. P.J.Joseph Francis, Rani Joseph and K.E.George, Intern. J. Polymeric Mater., 38, 65-78 (1997).

24. B.Elbirli , J.T.Lindt, S.R.Gottgetreu and S.M.Baba, Polym. Engg. Sci., 23(2), 86 (1983).

25. P.J.J.Francis, R.Joseph and K.E.George, Kaut. Gummi. Kunststoffe, 10, 704–709 (1997).

26. J.V.Fusco and P.Hous, "Rubber Technology—Butyl and Harobutyl Rubbers", M.Morton, Ed., Van Nostrand Reinhold, New York, 3rd Edn., Chapter 10 (1987).

27. Krzysztof Wilczynski, "Evaluating Screw Performance in Extrusion", Nicholas P. Chereminisof (Ed.), Marcel Dekker Inc. NY, Chap. 3 (1983).

28. G.Schenkel, Kunststoffe 60, 52 (1970).

29. Z.Tadmor and I.Klein, "Engineering Principles of Plasticating Extrusion", Van Nostrand Reinhold, New York, Chapter 9 (1970).

30. T.Colelough, J.I.Cunnen and G.M.C.Higgins, J. Appl. Polym. Sci., 12, 295 (1968).

31. A.G.Vieth, J. Polym. Sci., 25, 355 (1957).

32. D.S.Campbell, J. Appl. Polym. Sci., 14, 1409 (1970).

33. N.G.Kumar, J. Polym. Sci. Rev., 15, 255-325 (1980).

34. D.R.Saini and A.V.Shenoy, J. Elast. Plast., 17, 189-217 (1985).

35. Z.Komblowski and Turzecki, Rheol. Acta, 22, 34-40 (1983).

36. A.V.Chapman and M.Porter, "Natural Rubber Science and Technology, A.D.Roberts Ed., Oxford University Press, Oxford, Chap. 12 (1988).

37. P.J.Joseph Francis, Rani Joseph and K.E.George, Iranian Polymer Journal, 6, 19-25 (1997).

CHAPTER 4

STARVED EXTRUSION FOR THE IMPROVEMENT OF MECHANICAL PROPERTIES OF FILLED NR, SBR AND IIR VULCANIZATES

Parts of work presented in this chapter have been published in Journal of Elastomers and Plastics, 29(2), 148–162 (1997) and Iranian Polymer Journal, 6(1), 19–26 (1997).

STARVED EXTRUSION FOR THE IMPROVEMENT OF MECHANICAL PROPERTIES OF FILLED NR, SBR AND IIR VULCANIZATES

4.1 INTRODUCTION

In view of the fact that the feeding rate in single screw extrusion of natural and synthetic gum rubber compounds influences the mechanical properties of their vulcanizates, in this part of the study, we propose to investigate the effect of feeding rate in the extrusion of the corresponding filled rubber compounds. Filled rubber vulcanizates are commercially more important since fillers are generally incorporated in almost all rubber products for improved processability, reinforcement, or cost reduction. Carbon black was chosen as the filler since it is the most widely used filler for commercial rubber products.

4.2 EXPERIMENTAL

Extrusion studies were performed on a laboratory extruder attached to a Brabender plasticorder model PL2000 with an L/D ratio 10 and compression ratio of 1 and provided with a feeding roll. The formulations of the filled compounds of NR, SBR and IIR selected for the study are shown in Table 4.1.

A laboratory two-roll mill was used to prepare the compounds according to ASTM standards. The compounds were sheeted out by

Table 4:1 Formulations of the compounds

	NR filled compound	SBR filled compound	IIR filled compound
NR	100	--	--
SBR	--	100	--
IIR	--	--	100
Zinc oxide	5	4.0	4.0
Stearic acid	2.0	1.5	2.0
Antioxidant (Pilflex-13)	1	1	1
HAF Black (N-330)	50	45	45
Aromatic oil	7.0	6.0	--
Paraffinic oil	--	--	7.5
Dibenz thiazyl disulphide (MBTS)	0.6	--	0.5
Tetramethyl thiuram disulphide (TMTD)	--	0.25	1.0
N-cyclohexyl-2-benzthiazyl sulphenamide (CBS)	--	0.8	--
Sulphur	2.5	2.0	1.5

passing through a 1 mm nip of the mixing mill. For feeding into the extruder, the sheets were cut into 10 mm strips. By placing different number of layers of the strips on the feeding roll, the feeding rates were adjusted.[1] The feeding rates were measured by the rate of output of the extrudate.[2] The compounds were extruded at varying feeding rates mainly in the starve fed regions at 20, 40, 60 and 80 rpm and at different temperatures. The torque values corresponding to various feeding rates at above rpms and temperatures were noted.

After extrusion of NR, SBR and IIR filled compounds, the cure curves of the compounds were taken on a Goettfert elastograph model 67.85 according to relevant ASTM standards at 150°C for NR and SBR and at 170°C for IIR. The extruded samples were vulcanized upto their optimum cure times (the time required for attaining 90% of the maximum torque) in an electrically heated laboratory hydraulic press. The moulded samples were then cooled by immersing in water. Dumbbell specimens were cut out of the sheets in the milling/extrusion and transverse directions for tensile testing. A Zwick universal testing machine model 1445 was used to measure the tensile properties of the vulcanizates at an extension rate 500 mm/min. as per ASTM standards. Tear strength of selected vulcanizates were measured on the Zwick UTM by using angular test specimens prepared from the compression moulded sheets. Samples for compression set and hardness were moulded and tested as per relevant ASTM standards. The ageing resistance of selected vulcanizates was

studied after ageing the samples at 100°C for 48 hours in a laboratory air oven. The retention in the tensile properties of the aged samples was then measured.

From noting feeding rates at the flood fed level and at different starve fed levels the percentage of starvation was calculated.[3] The fluctuations in temperature and flow rate at certain starvation levels, flood feeding and force feeding levels during extrusion were noted. The densities of selected starve fed, flood fed and force fed samples of filled NR, SBR and IIR extruded vulcanizates were measured.

. In the case of filled NR and SBR vulcanizates the swelling index was measured by equilibrium swelling in toluene, and in the case of filled IIR vulcanizates by equilibrium swelling in benzene according to the following equation

$$\text{Swelling index} = \frac{\text{Swollen weight} - \text{Deswollen weight}}{\text{Initial weight}}$$

From the equilibrium swelling data the average chemical crosslink density of a few sets of starve fed, flood fed and force fed samples of NR, SBR and IIR vulcanizates was estimated.[4] The crosslink density $1/2M_c$ was determined from V_r using the Flory–Rehner equations.[5,6] By using a Brookfield viscometer the viscosity values of solutions of extruded NR, SBR and IIR compounds were measured. By using a thermogravimetric analyser,

Du–Pont 2000, the TGA traces of starve fed, flood fed and force fed compounds of NR, SBR and IIR were taken.

The percentage bound rubber content (filler gel) of a few sets of samples were determined by immersing the samples in 25 ml of a suitable solvent (toluene for NR and SBR and benzene for IIR) for seven days at room temperature (solvent was renewed after three days). Then the sample was dried for one day in air at room temperature and then for 24 hours in an oven at 105°C. The percentage bound rubber of the corresponding rubber vulcanizates was calculated as described in chapter 2.

For investigating the carbon black dispersion, the vulcanizate specimens were sandwitched between two rectangular glass sample holders and observed under the microscope with a magnification of 30 and photographs were taken using a polaroid MP4 land camera.

The tensile fracture surfaces of a few typical samples were examined using a scanning electron microscope to study the mode of failure.

4.3 RESULTS AND DISCUSSION

4.3.1 Torque

The variation of torque with feeding rate for filled NR, SBR and IIR for different rpms of 20, 40, 60 and 80 and at a constant temperature of 80°C is shown in the Fig.4.1. It is noticed that extrusion torque substantially reduces with increase in the starvation level. The percentage reduction in torque between the flood feeding point and the lowest starve feeding point was upto 31%.

The variation of torque with feeding rate for filled NR, SBR and IIR at different temperatures and at a fixed rpm of 40 is shown in Fig.4.2. It may be found that torque gets progressively reduced with increase in starvation level. The percentage reduction in torque between the flood feeding point and the lowest starve feeding point is upto 34%. In the case of filled compounds, the torque required at any stage of the extrusion is found to be higher than that of the corresponding gum rubber compounds as expected. It can be concluded from the Figs. 4.1 and 4.2 that the extrusion torque can be progressively decreased by operating in the starved region or employing higher temperatures. The variation of reduction in torque with percentage of starvation at different rpms and different temperatures is shown in Table 4.2.

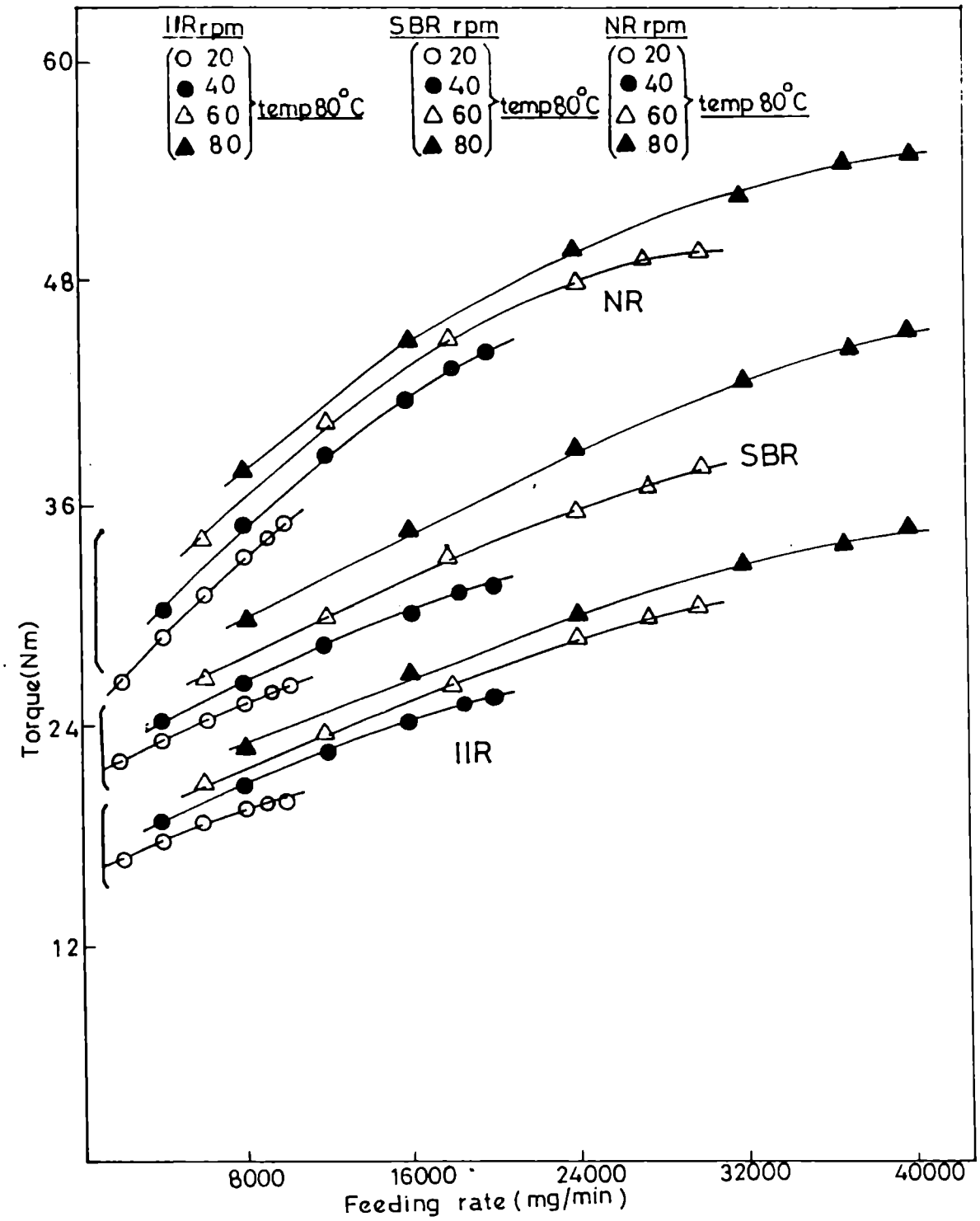


Fig.4.1: Variation of torque in the extrusion of filled NR, SBR and IIR compounds with feeding rate at different rpms.

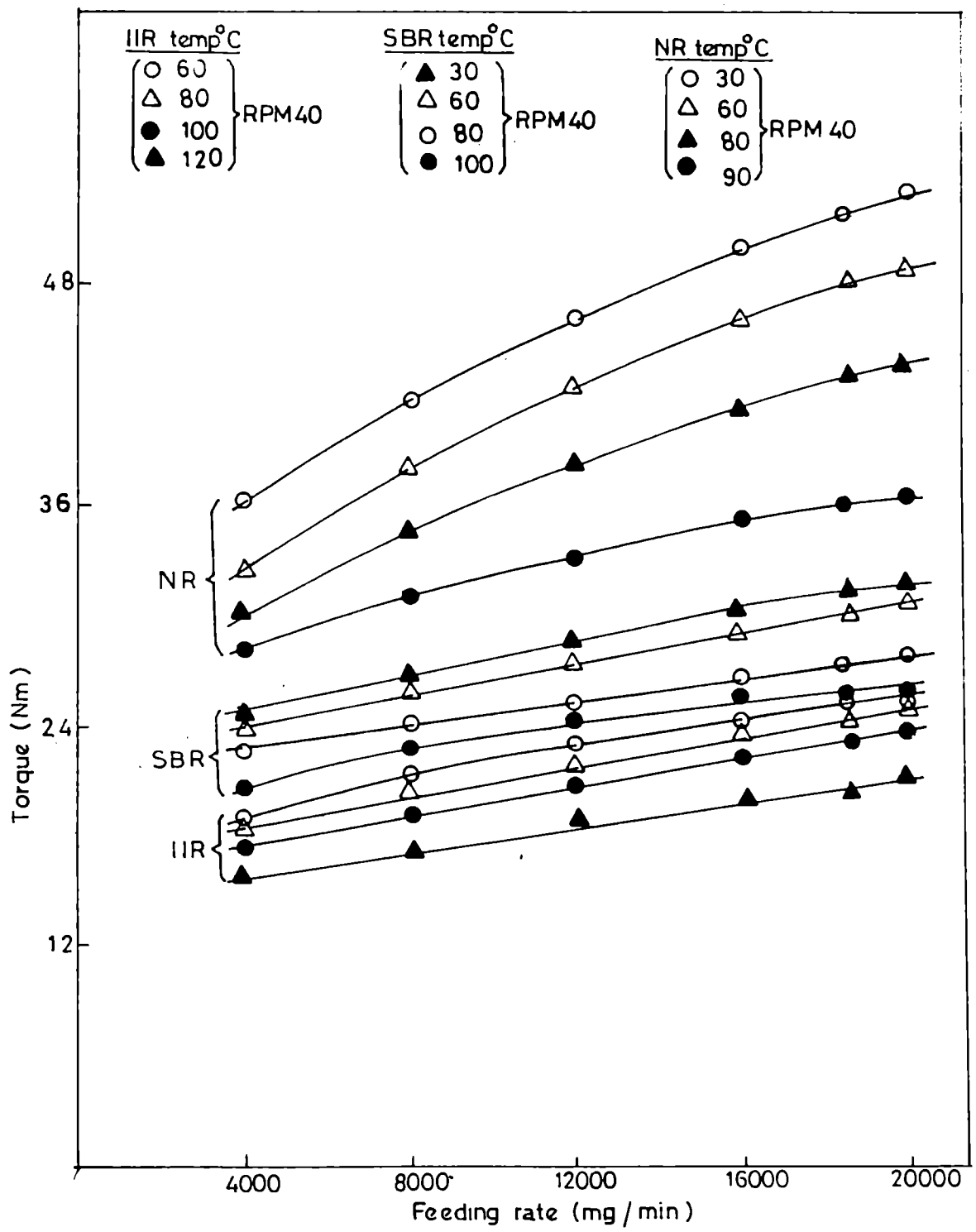


Fig.4.2: Variation of torque in the extrusion of filled NR, SBR and IIR compounds with feeding rate at different temperatures.

Table 4.2: Variation of the percentage reduction in torque with percentage of starvation of filled NR, SBR and IIR compounds

% Starvation	% Reduction in Torque at 20 rpm at 80°C			% Reduction in Torque at 80 rpm and 80°C			% Reduction in Torque at 40 rpm at 60°C			% Reduction in Torque at 40 rpm at 100°C		
	NR	SBR	IIR	NR	SBR	IIR	NR	SBR	IIR	NR	SBR	IIR
80	27.4	28.2	31.3	26.4	28.7	30.9	24.4	25.7	29.8	29.3	30.4	34.2
50	18.6	20.9	23.4	19.4	20.9	22.1	17.0	19.3	21.4	21.1	23.0	25.6
30	13.5	14.8	16.7	13.4	14.2	15.1	12.1	13.0	14.5	15.3	15.5	17
10	10.9	11.5	12.8	9.8	10.2	10.6	10.5	10.8	11.9	11.6	13.0	14.1
0 (Flood feeding)	--	--	--	--	--	--	--	--	--	--	--	--

4.3.2 Mechanical properties.

4.3.2.1 Tensile properties

The variation of tensile strength with feeding rate for NR, SBR and IIR filled vulcanizates in the milling/extrusion direction at different rpms at 80°C is shown in the Fig.4.3. The maximum feeding rate in each curve in the figure corresponds to the force fed point. The feeding rate just below the force fed point represents the flood feeding point and the other feeding rates are in the starve fed region.

It is noticed that the tensile strength increases initially with feeding rate, reaches a maximum value and decreases thereafter in the case of NR, SBR and IIR filled vulcanizates, irrespective of rpm. This leads to the conclusion that there is a particular feeding rate in the starved region, which results in maximum tensile strength. This is in accordance with the result obtained for gum vulcanizates of NR, SBR and IIR.

Figure 4.4 shows the variation of tensile strength of filled NR, SBR and IIR vulcanizates with feeding rate in transverse direction at different rpm at 80°C. The higher difference between the tensile strength measured in the milling/extrusion and transverse directions (Figs. 4.3 and 4.4) especially at the low levels of starvation clearly shows the preferential orientation effect at this feeding rate. As in the case of gum vulcanizates, the preferential orientation effect is more pronounced in

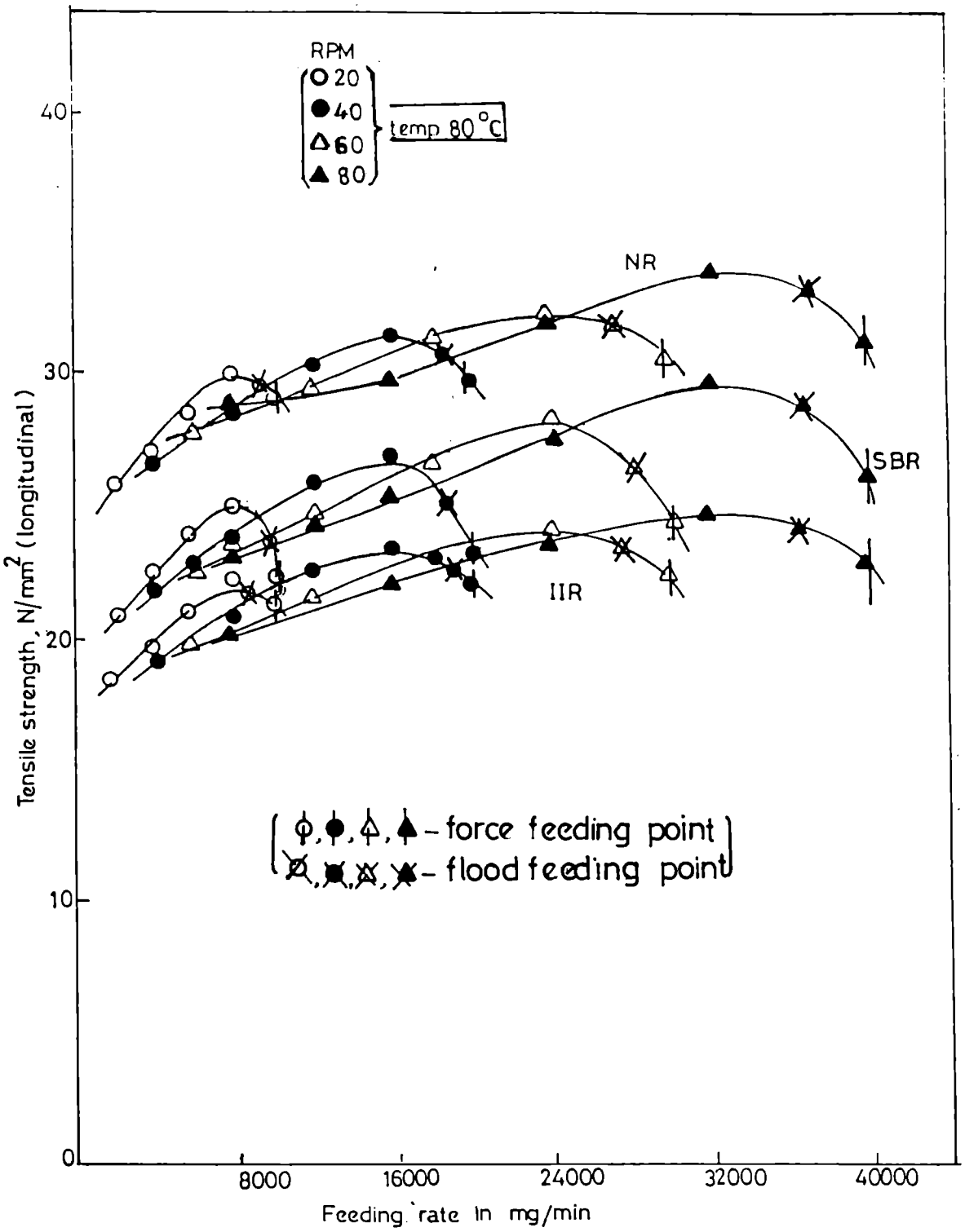


Fig.4.3: Variation of tensile strength of filled NR, SBR and IIR vulcanizates with feeding rate at different rpms in milling/extrusion direction.

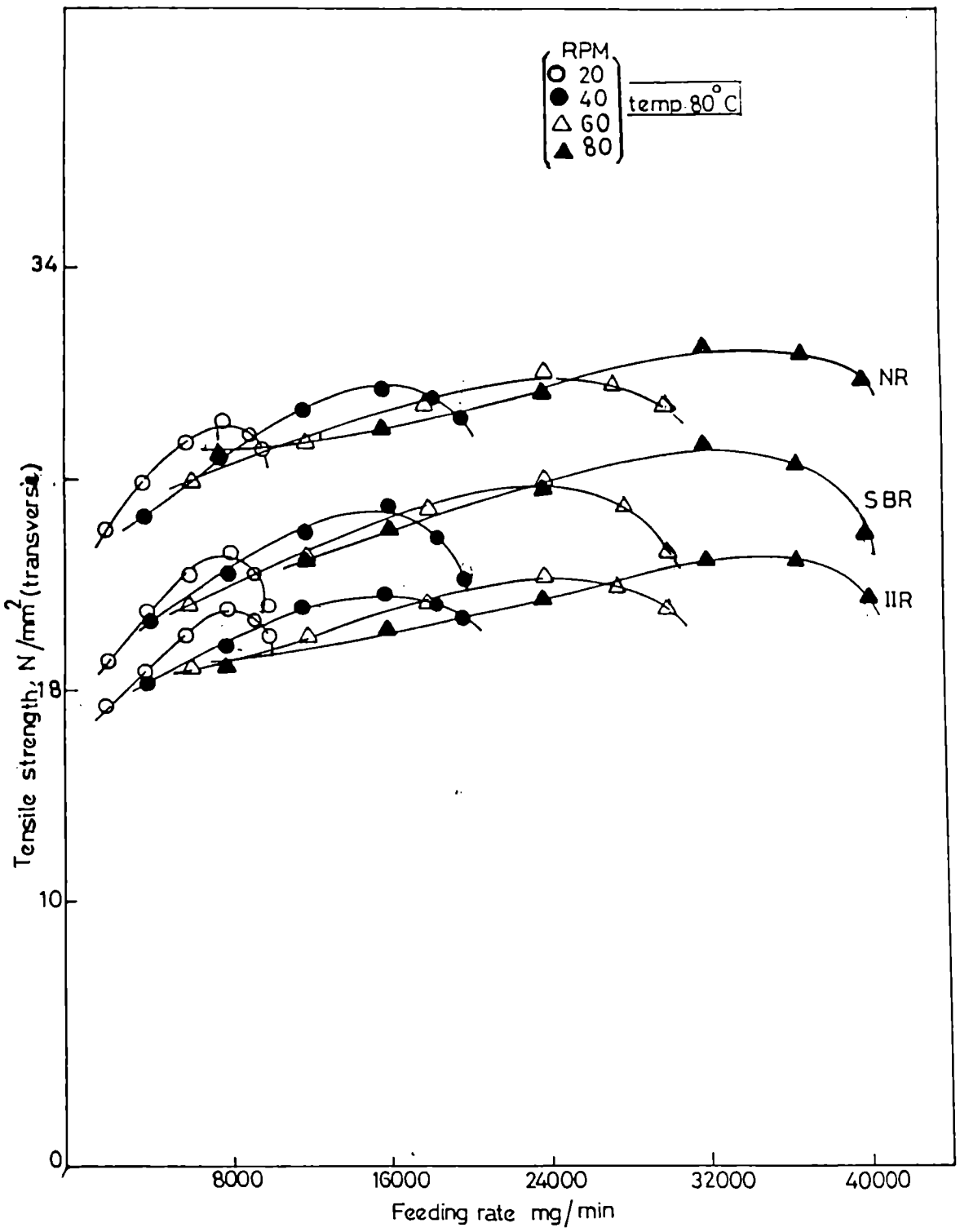


Fig.4.4: Variation of tensile strength of filled NR, SBR and IIR vulcanizates with feeding rate at different rpms in transverse direction.

filled NR vulcanizates compared to filled SBR and IIR vulcanizates. This may be due to the crystalline nature of NR. After the starve feeding point at which maximum tensile strength is observed, the tensile strength decreases with feeding rate at flood feeding point and force feeding point (in Figs. 4.3 and 4.4).

The variation in elongation at break of filled NR, SBR and IIR vulcanizates with feeding rate in milling/extrusion and transverse directions at different rpms is shown in Figs.4.5 and 4.6. Here also the elongation at break initially increases with feeding rate, reaches a maximum value in the starved region for each rpm and thereafter decreases as in the case of gum vulcanizates. This shows that there is a particular feeding rate in the starved region, which results in maximum elongation at break. The simultaneous increase in the tensile strength and elongation at break of the extrudates at a particular level of starvation expresses the uniform shear and lower mechanical break-down at this feeding rate.[7,8]

Figures 4.7 and 4.8 represent the variation in tensile strength of NR, SBR and IIR filled vulcanizates with feeding rate in the milling/extrusion and transverse directions at different temperatures at a fixed rpm. In the case of NR, the tensile strength increases with the temperature in the range of 30°C to 90°C. From 100°C onwards thermal degradations seems to control the situation and this leads to the

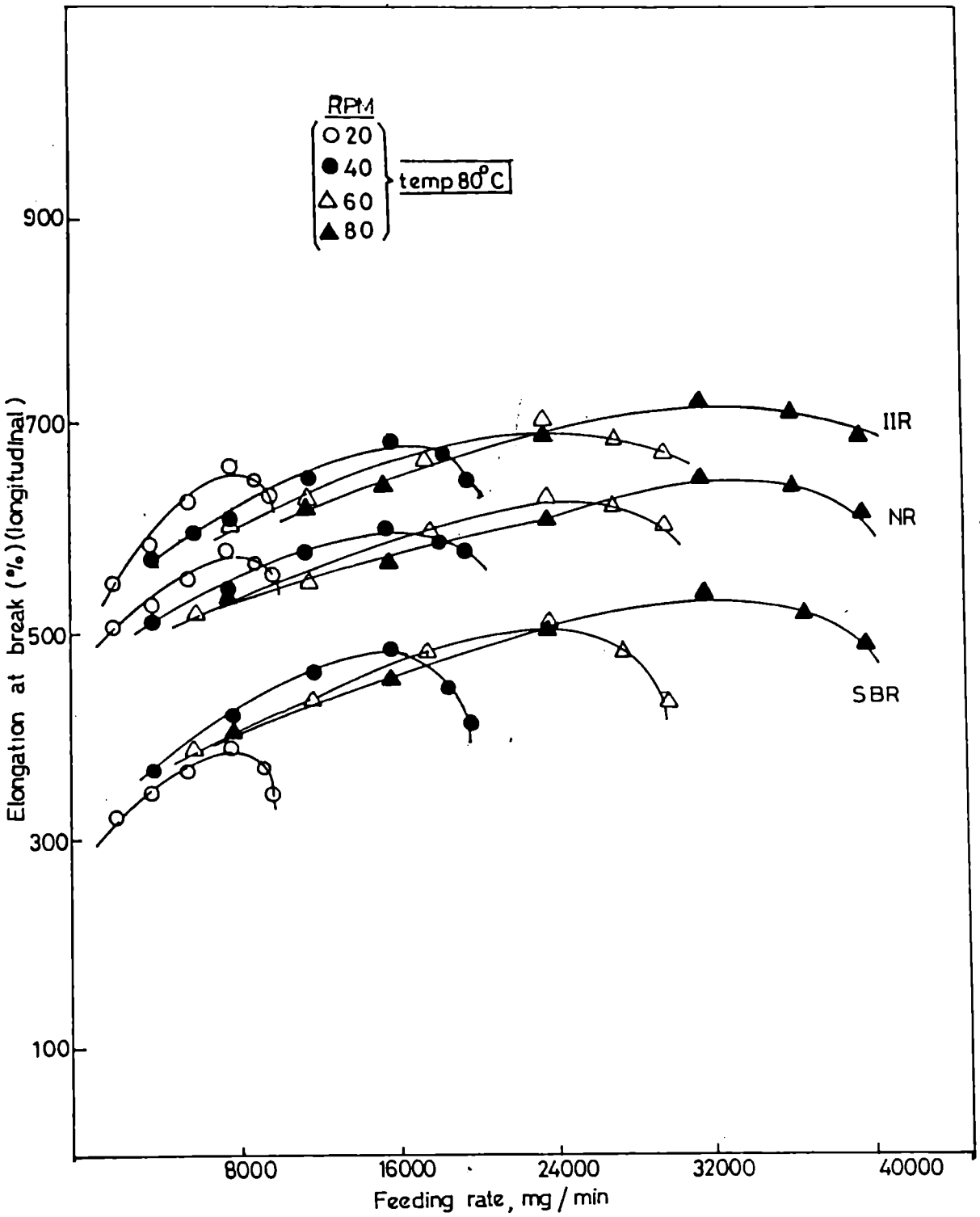


Fig.4.5: Variation of elongation at break of filled NR, SBR and IIR vulcanizates with feeding rate at different rpms in the milling/extrusion direction.

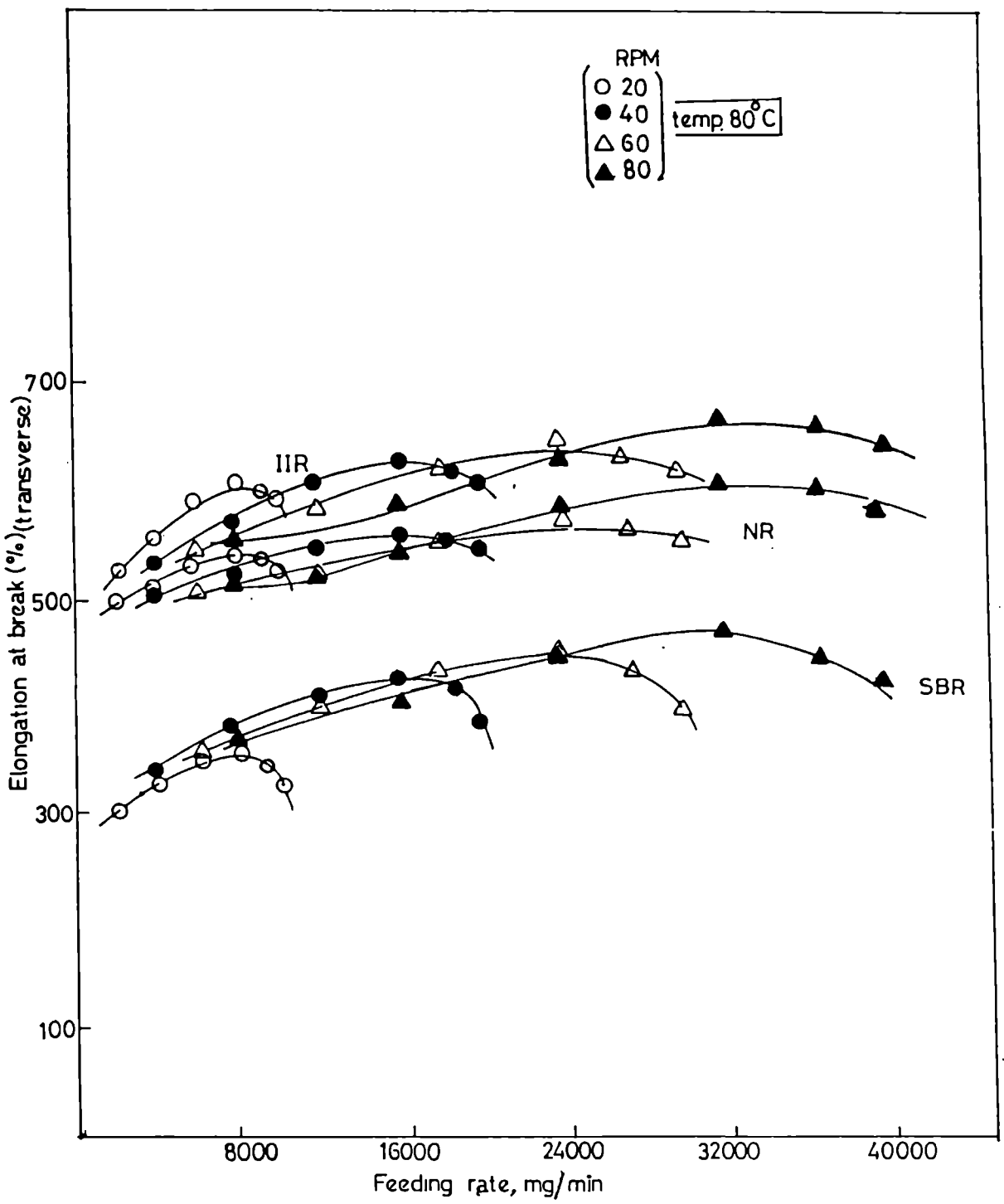


Fig.4.6: Variation of elongation at break of filled NR, SBR and IIR vulcanizates with feeding rate at different rpms in the transverse direction.

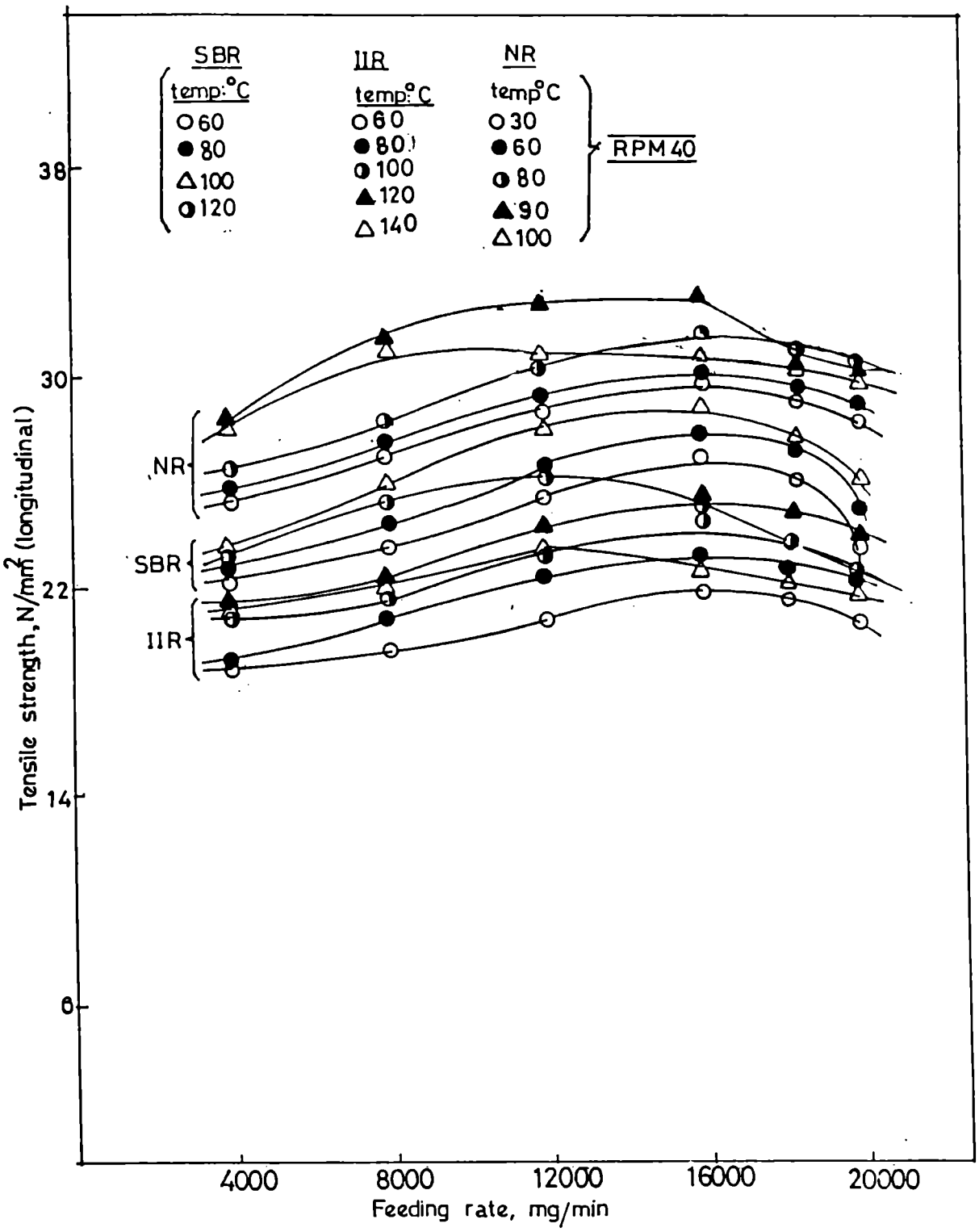


Fig.4.7: Variation of tensile strength of filled NR, SBR and IIR vulcanizates with feeding rate at different temperatures in the milling/extrusion direction.

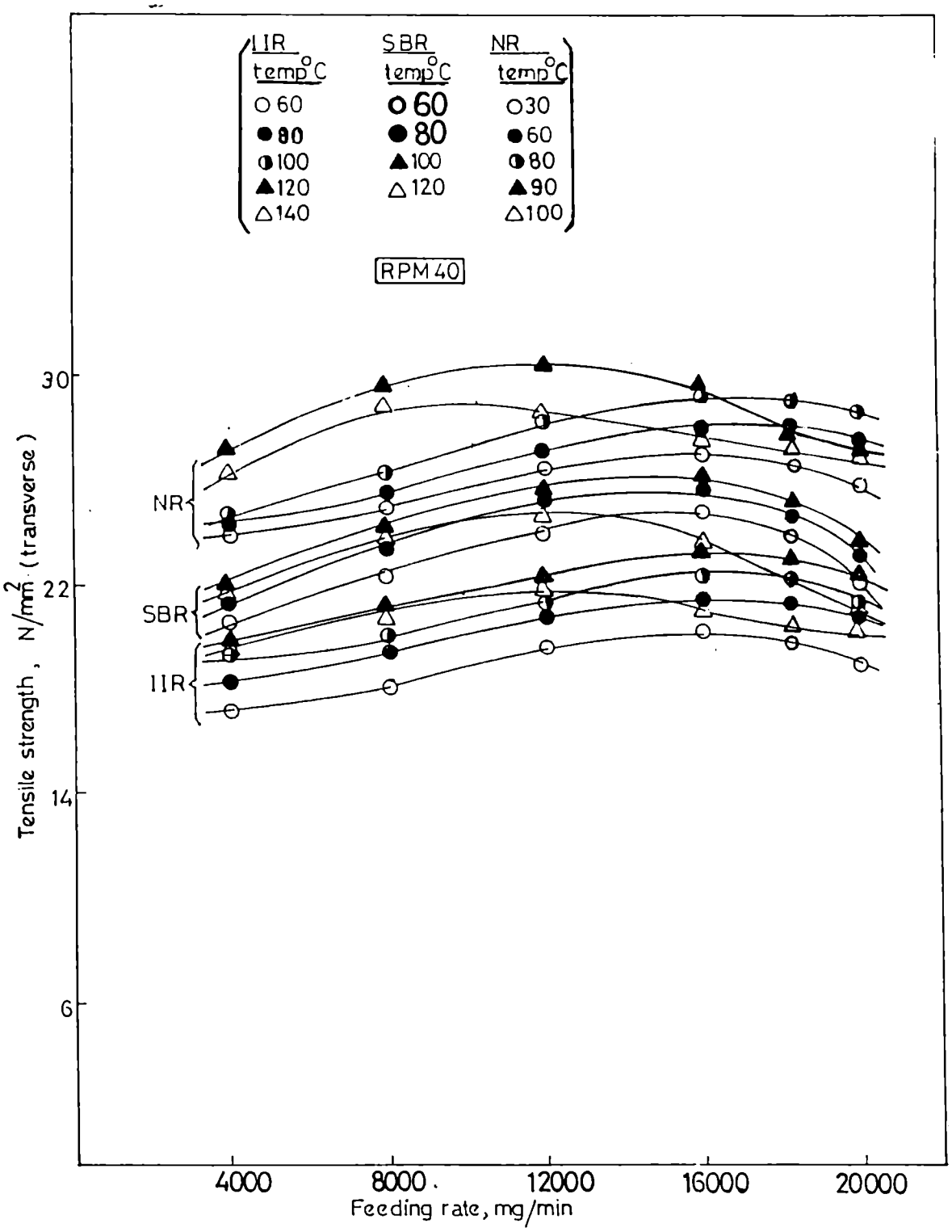


Fig.4.8: Variation of tensile strength of filled NR, SBR and IIR vulcanizates with feeding rate at different temperatures in the transverse direction.

deterioration in the tensile strength. In the case of SBR which is more thermally stable than NR, the tensile strength improves with the temperature when it is raised from 60°C to 100°C showing that deterioration due to thermal degradation is not controlling in this range. But the tensile strength at 120°C is less than that at 100°C showing the onset of degradation in the filled SBR vulcanizates. In the case of IIR, the tensile strength increases with temperature when it is raised from 60°C to 120°C. But the strength at 140°C is less than that at 120°C due to the onset of degradation.

The variation of elongation at break of filled NR, SBR and IIR vulcanizates with feeding rate at different temperatures at a fixed rpm in the milling/extrusion and transverse directions is shown in the Figs.4.9 and 4.10 respectively. The behaviour is almost similar to the variations of the tensile strength.

4.3.2.2 Tear strength, hardness and compression set

Figures 4.11 and 4.12 show the effect of feeding rate on the tear strength and hardness respectively of the filled NR, SBR and IIR vulcanizates at different rpms and temperatures. Both tear strength and hardness gradually increase with feeding rate and reach maximum values in the starve fed regions (just below the flood feeding point) and thereafter decrease at the flood feeding and force feeding points as in the case of tensile properties.

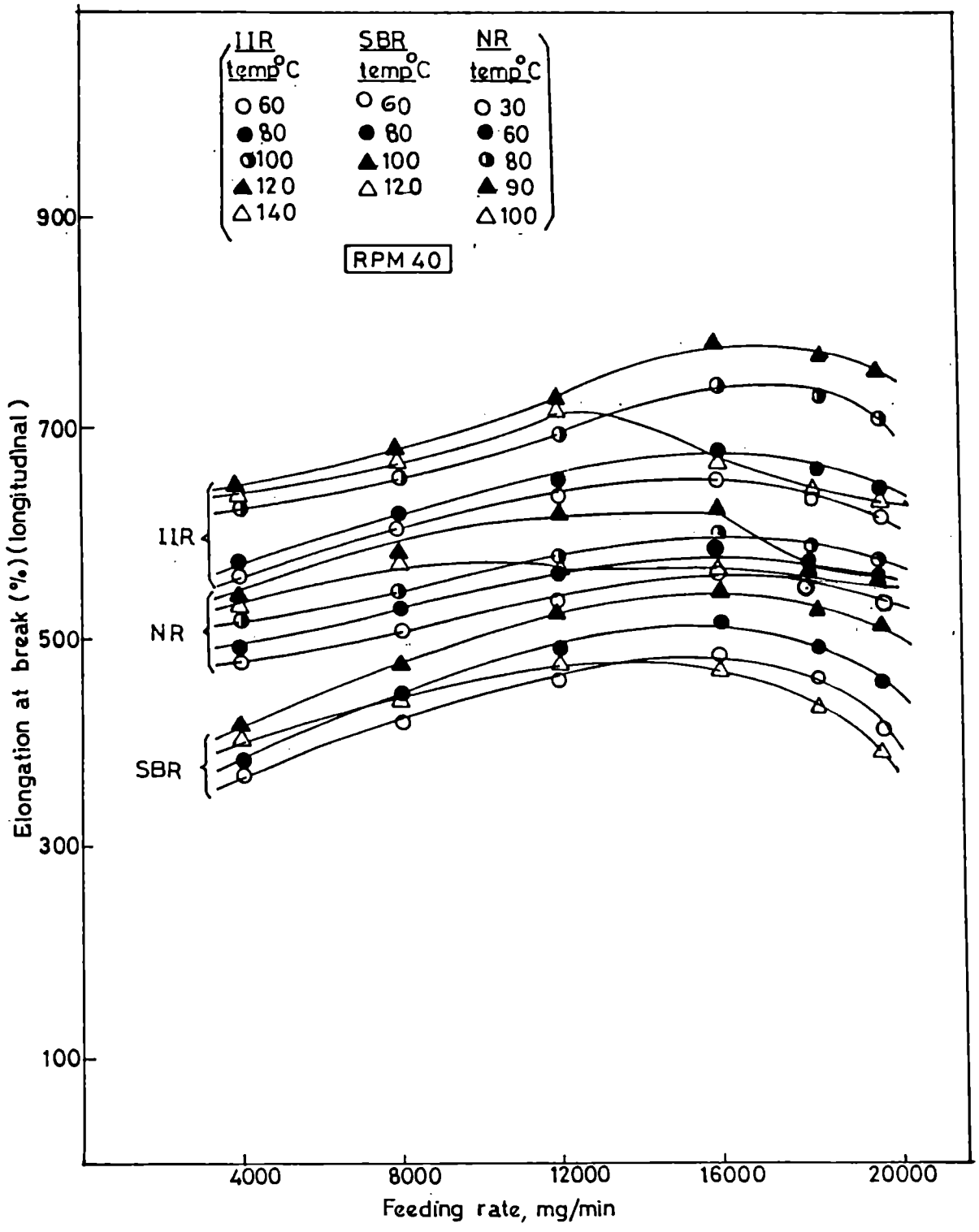


Fig.4.9: Variation of elongation at break of filled NR, SBR and IIR vulcanizates with feeding rate at different temperatures in the milling/extrusion direction.

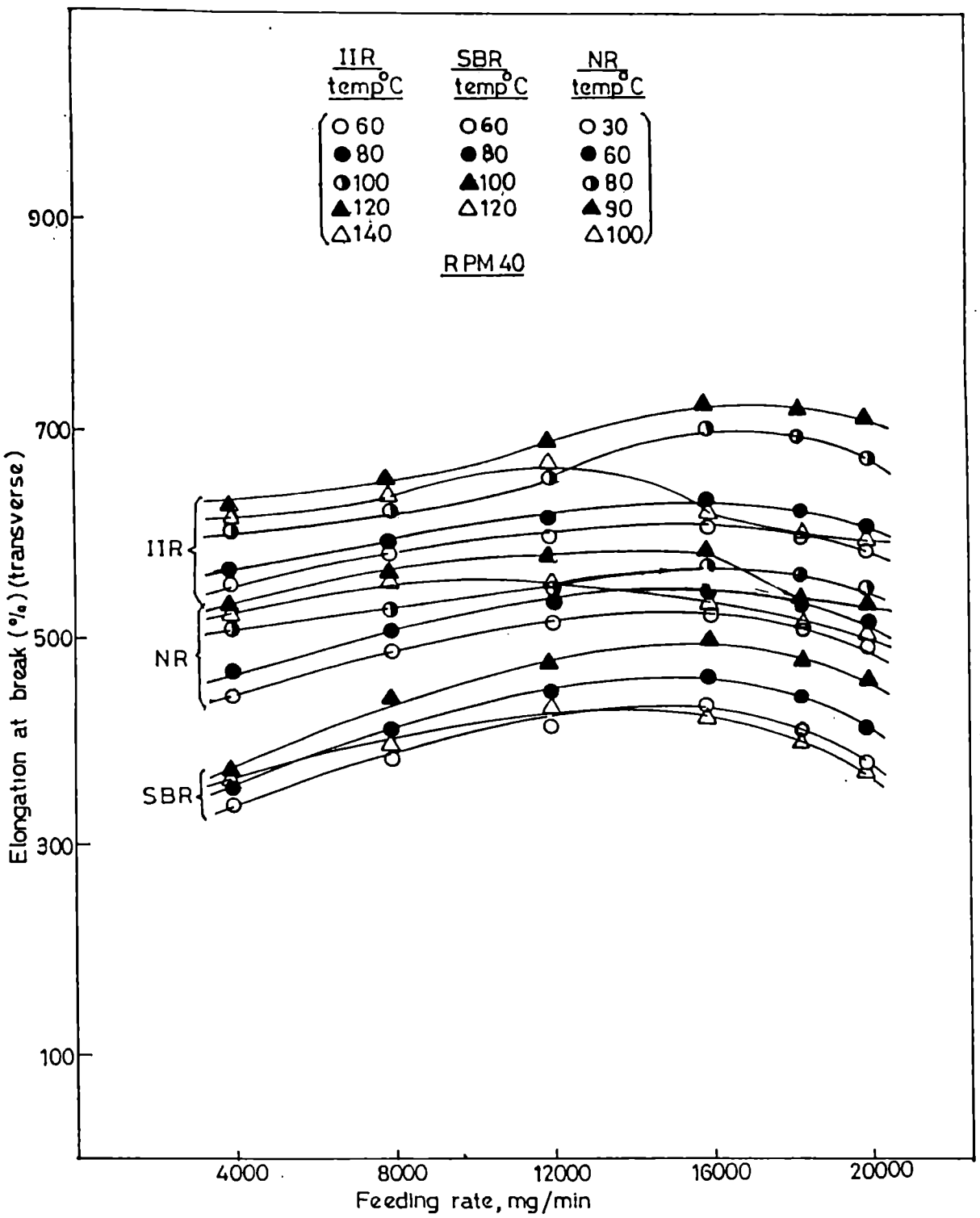


Fig.4.10: Variation of elongation at break of filled NR, SBR and IIR vulcanizates with feeding rate at different temperatures in the transverse direction.

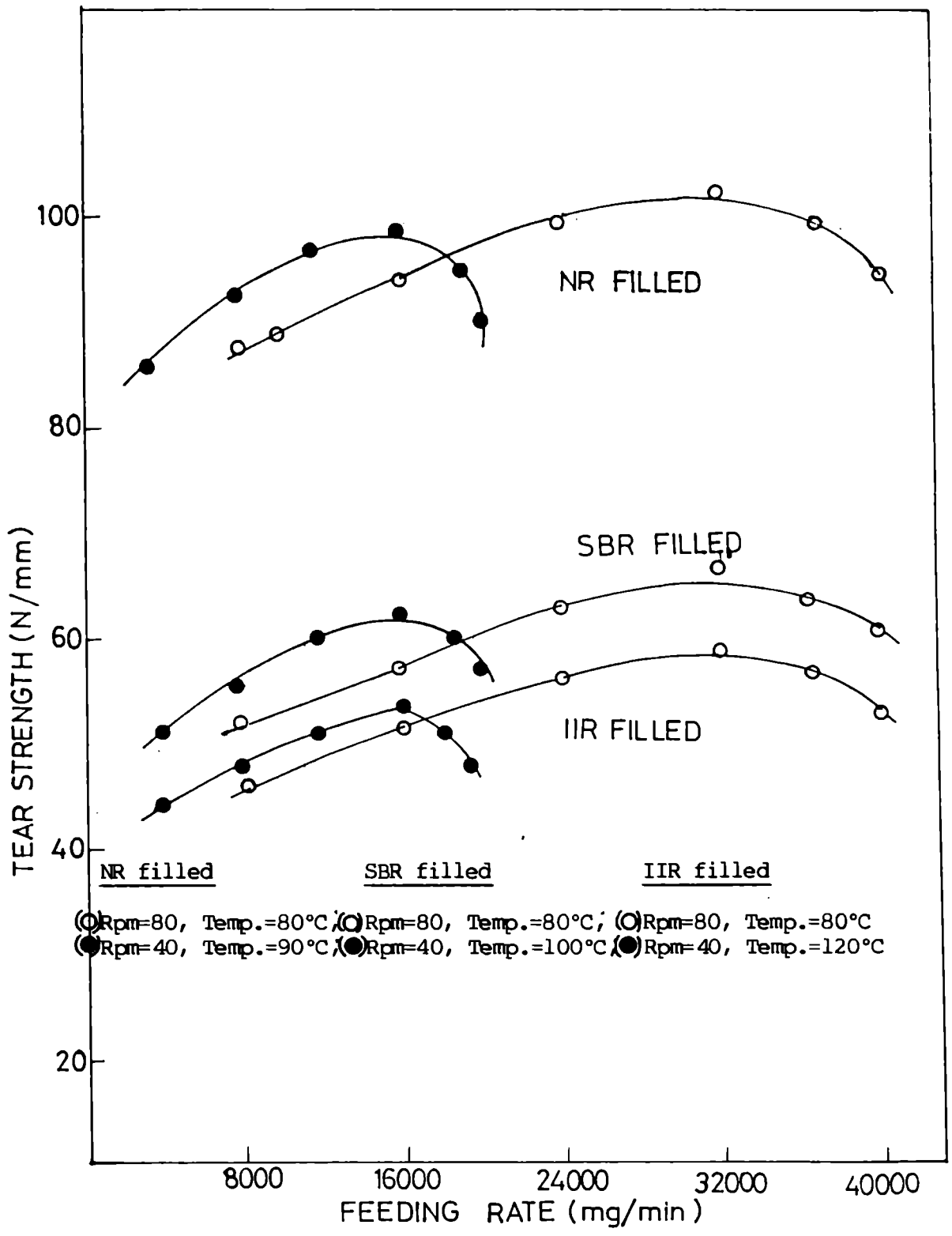


Fig.4.11: Variation of tear strength of filled NR, SBR and IIR vulcanizates with feeding rate at different rpms and temperatures.

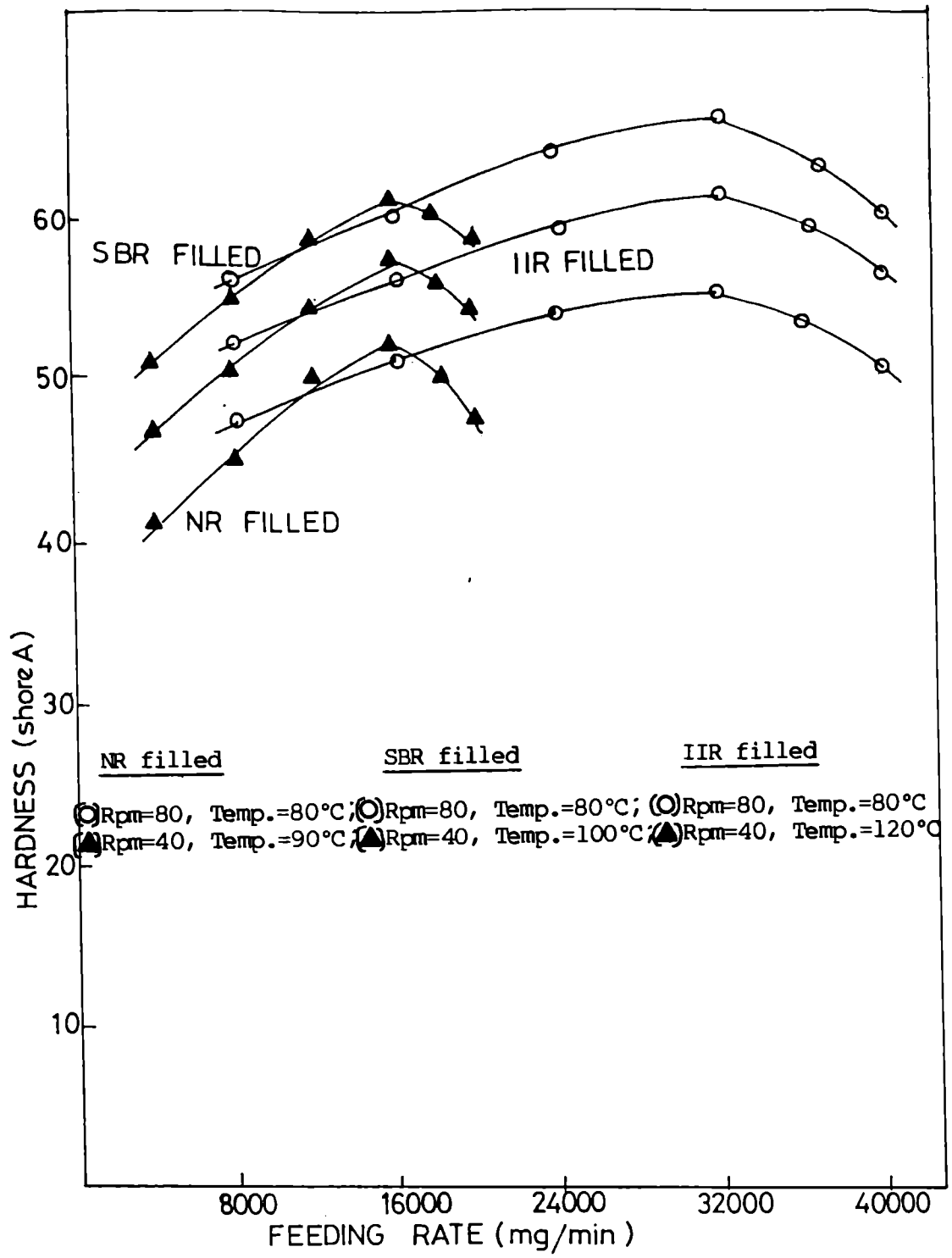


Fig.4.12: Variation of hardness of filled NR, SBR and IIR vulcanizates with feeding rate at different rpms and temperatures.

The variation of compression set with feeding rate of filled NR, SBR and IIR vulcanizates at two different rpms and temperatures is shown in the Fig.4.13. It is found that the compression set decreases with feeding rate, reaches a minimum value at the starve fed region and therafter increases from the flood feeding point upto the force feeding point. This may be due to higher degree of crosslinking[9,10] at the particular starve fed level than that at the flood fed, force fed levels and at higher levels of starving. The uniform temperature distribution and shear history of the compounds in starve feeding may be resulting in the higher degree of crosslinking[11,12]

4.3.3 Percentage of starvation and mechanical properties

The variation of tensile strength and elongation at break of filled vulcanizates of NR extruded compounds with percentage of starvation at different rpms and at a constant temperature of 80°C is shown in the Fig.4.14. It is noticed that when the rpm increases the percentage of starvation at which maximum properties are observed decreases. As in the case of vulcanizates of gum NR extruded compounds, maximum properties are obtained at percentage starvations of 14, 10, 9 and 8 respectively at rpms of 20, 40, 60, and 80 at a constant temperature of 80°C in the case of vulcanizates of filled NR extruded compounds too.

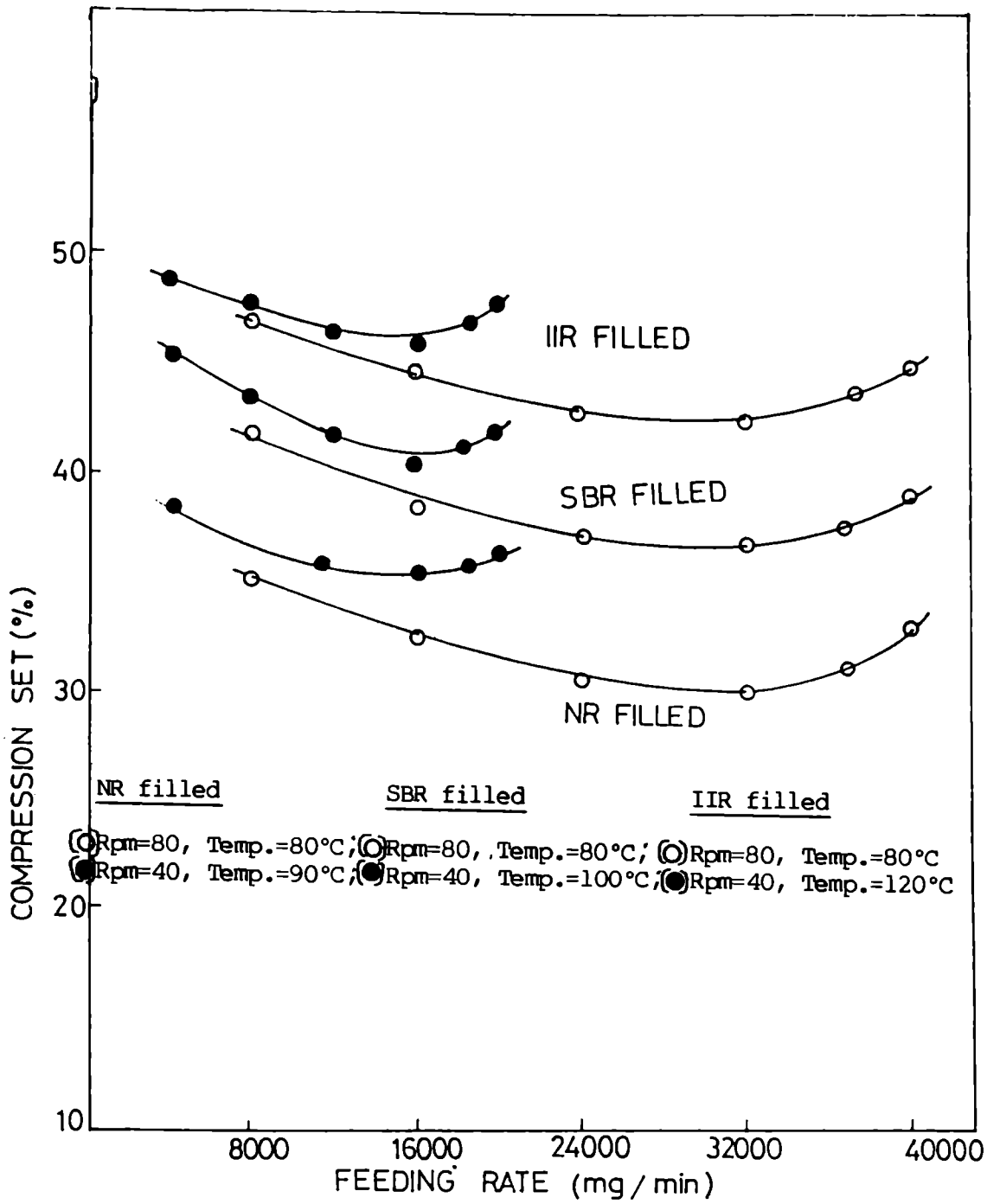


Fig.4.13: Variation of compression set of filled NR, SBR and IIR vulcanizates with feeding rate at different rpms and temperatures.

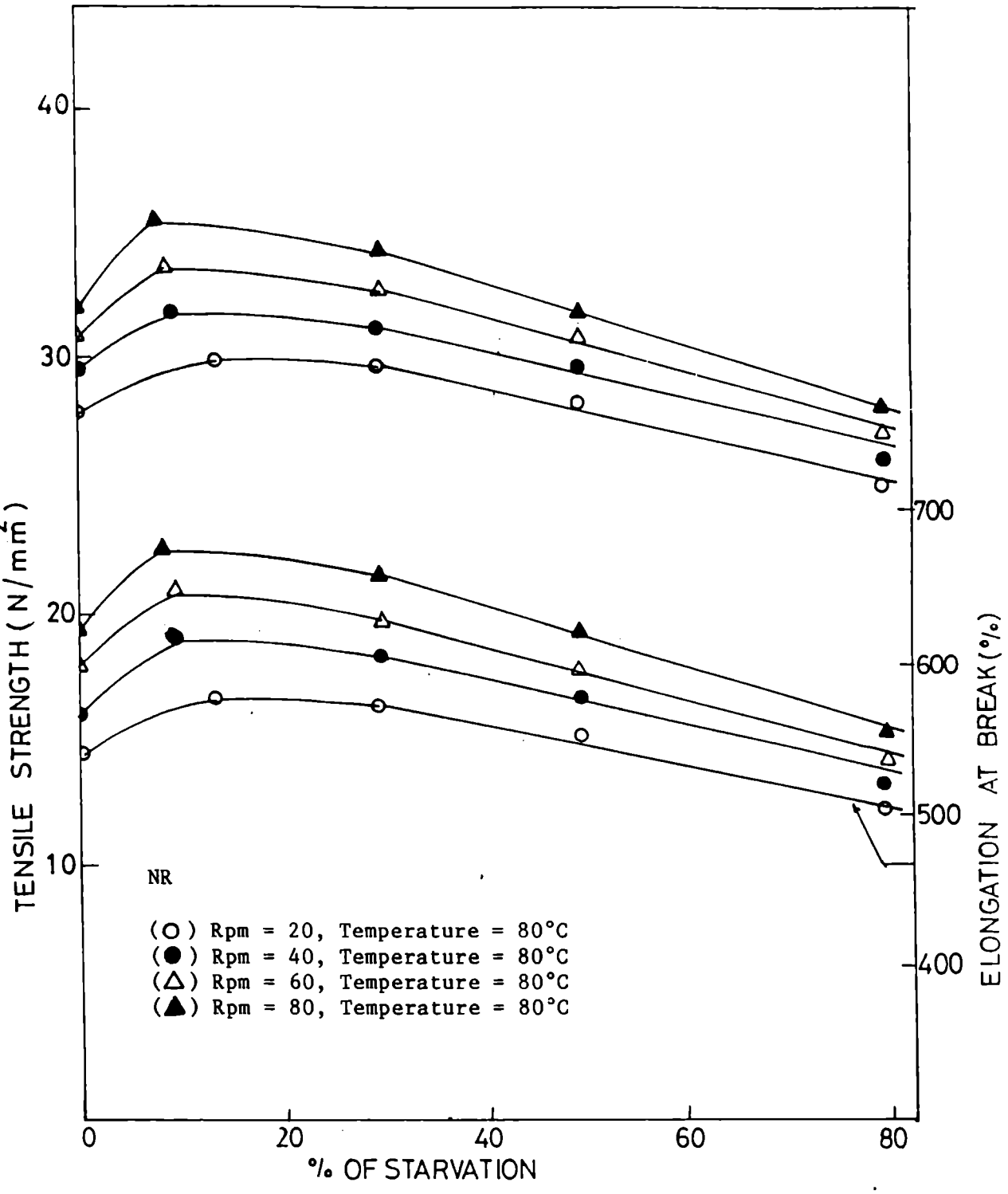


Fig.4.14: Variation of tensile strength and elongation at break of filled NR vulcanizates with percentage starvation at different rpms.

Figure 4.15 represents the variation of tensile strength and elongation at break of vulcanizates of filled NR extruded compounds, with percentage of starvation at different temperatures at a fixed rpm of 40. It is observed that the percentage of starvation at which maximum tensile properties are observed decreases with increase of temperature. Maximum properties are observed at percentage starvations of 15, 12, 10 and 9 respectively at temperatures of 30°C, 60°C, 80°C and 90°C at a fixed rpm of 40.

The variation of tensile properties of vulcanizates of SBR extruded compounds with percentage of starvation at different rpms and at a fixed temperature of 80°C is shown in the Fig.4.16. The percentage of starvation at which maximum properties are observed are 13, 11, 10 and 8 respectively at rpms of 20, 40, 60 and 80 at a constant temperature of 80°C.

The variation of tensile properties of vulcanizates of SBR extruded compounds with percentage of starvation at different temperatures and at a fixed rpm of 40 is shown in the Fig.4.17. At temperatures of 60°C, 80°C and 100°C, the maximum properties are obtained at percentage starvations of 12, 11 and 10 respectively.

Figure 4.18 shows the effect of percentage of starvation on the tensile properties of vulcanizates of IIR extruded compounds at different

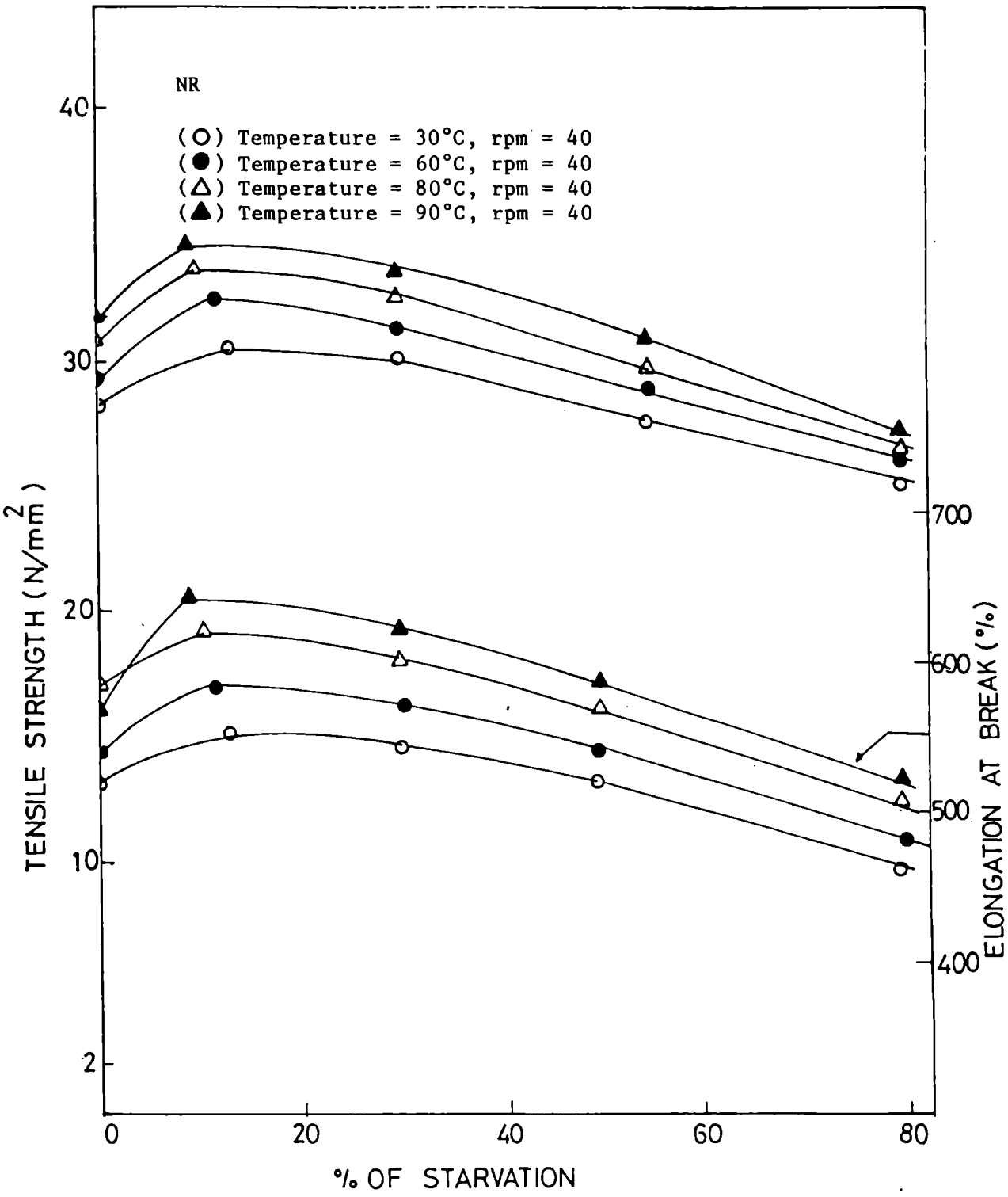


Fig.4.15: Variation of tensile strength and elongation at break of filled NR vulcanizates with percentage starvation at different temperatures.

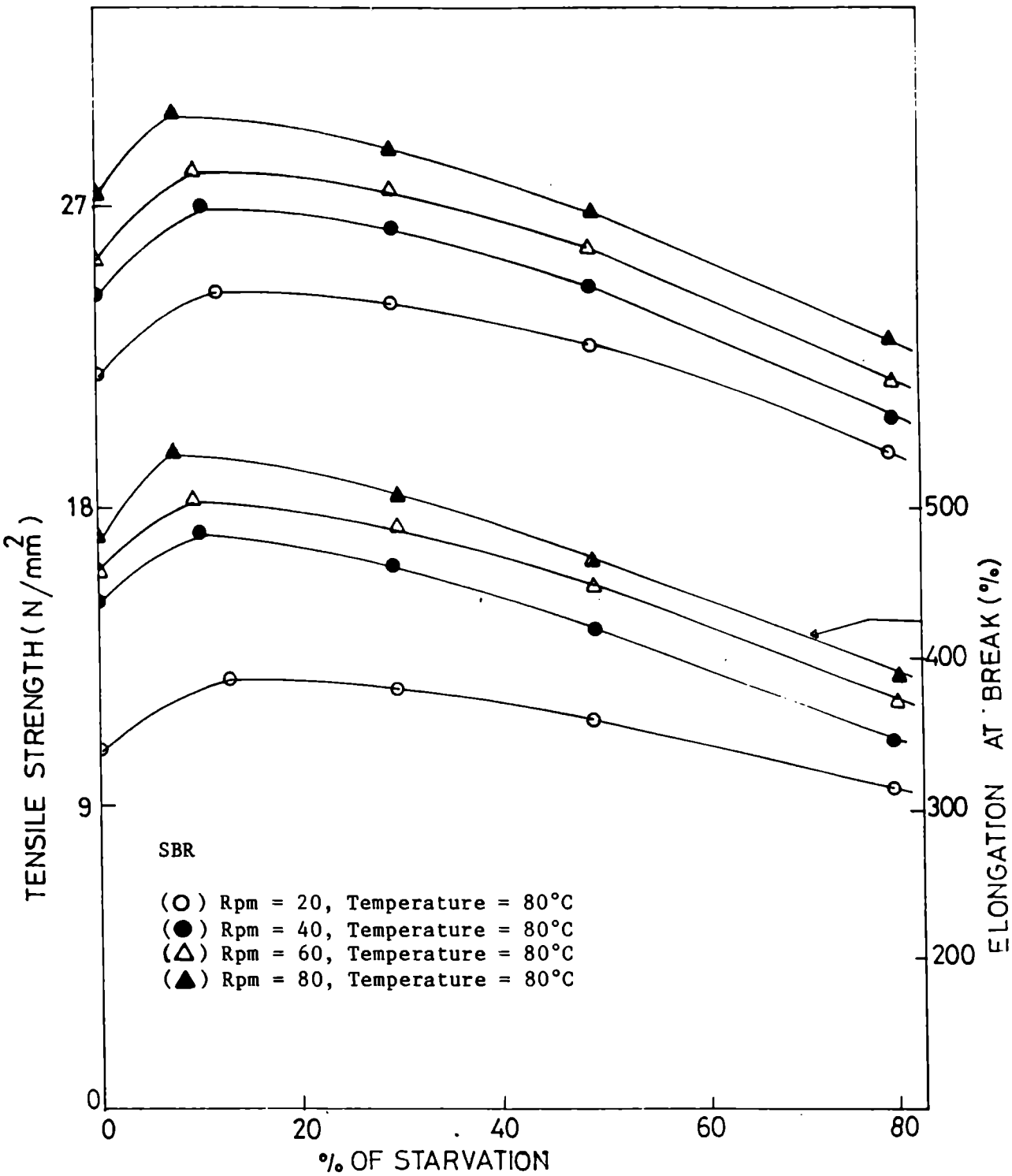


Fig.4.16: Variation of tensile strength and elongation at break of filled SBR vulcanizates with percentage starvation at different rpms.

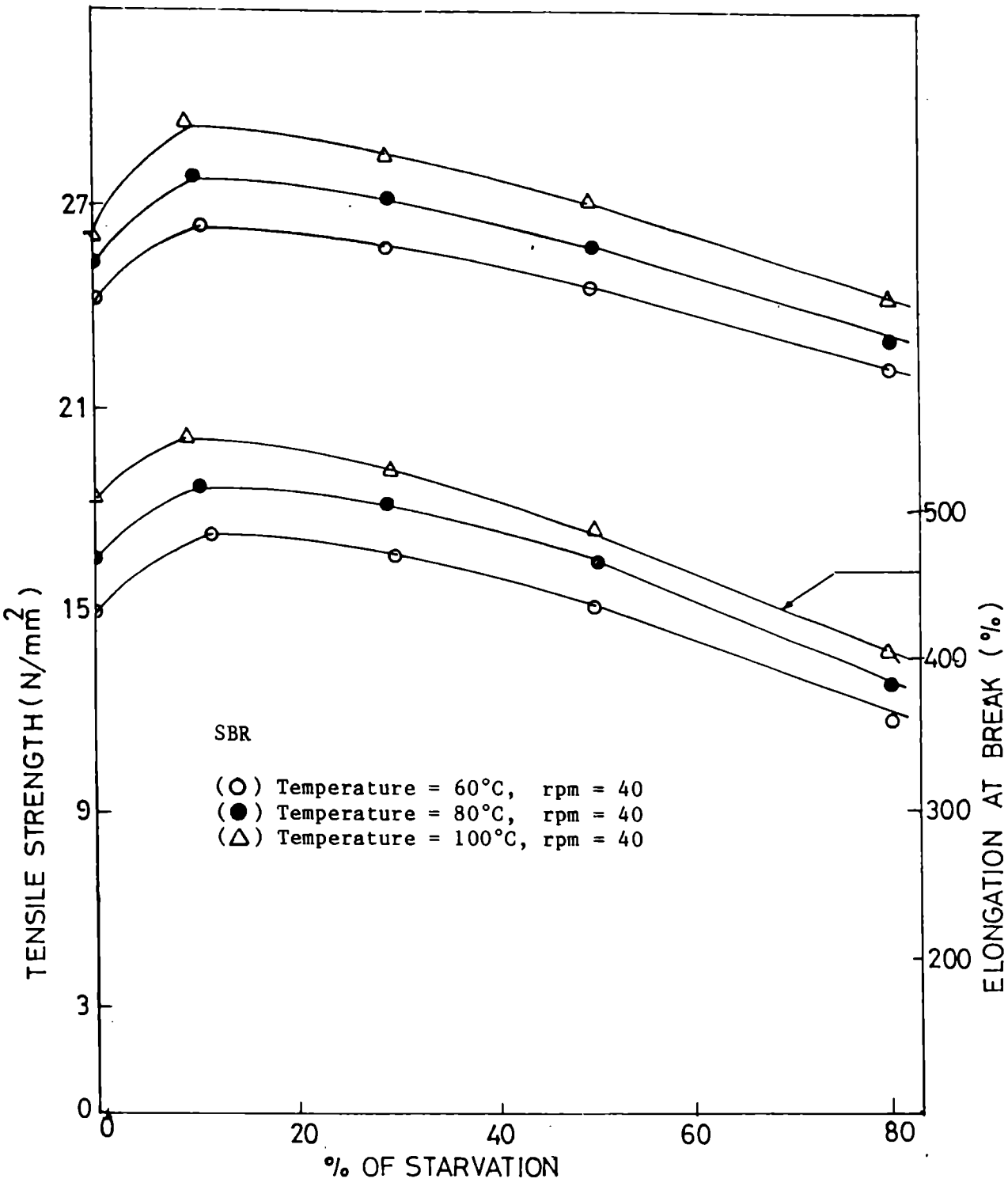


Fig.4.17: Variation of tensile strength and elongation at break of filled SBR vulcanizates with percentage starvation at different temperatures.

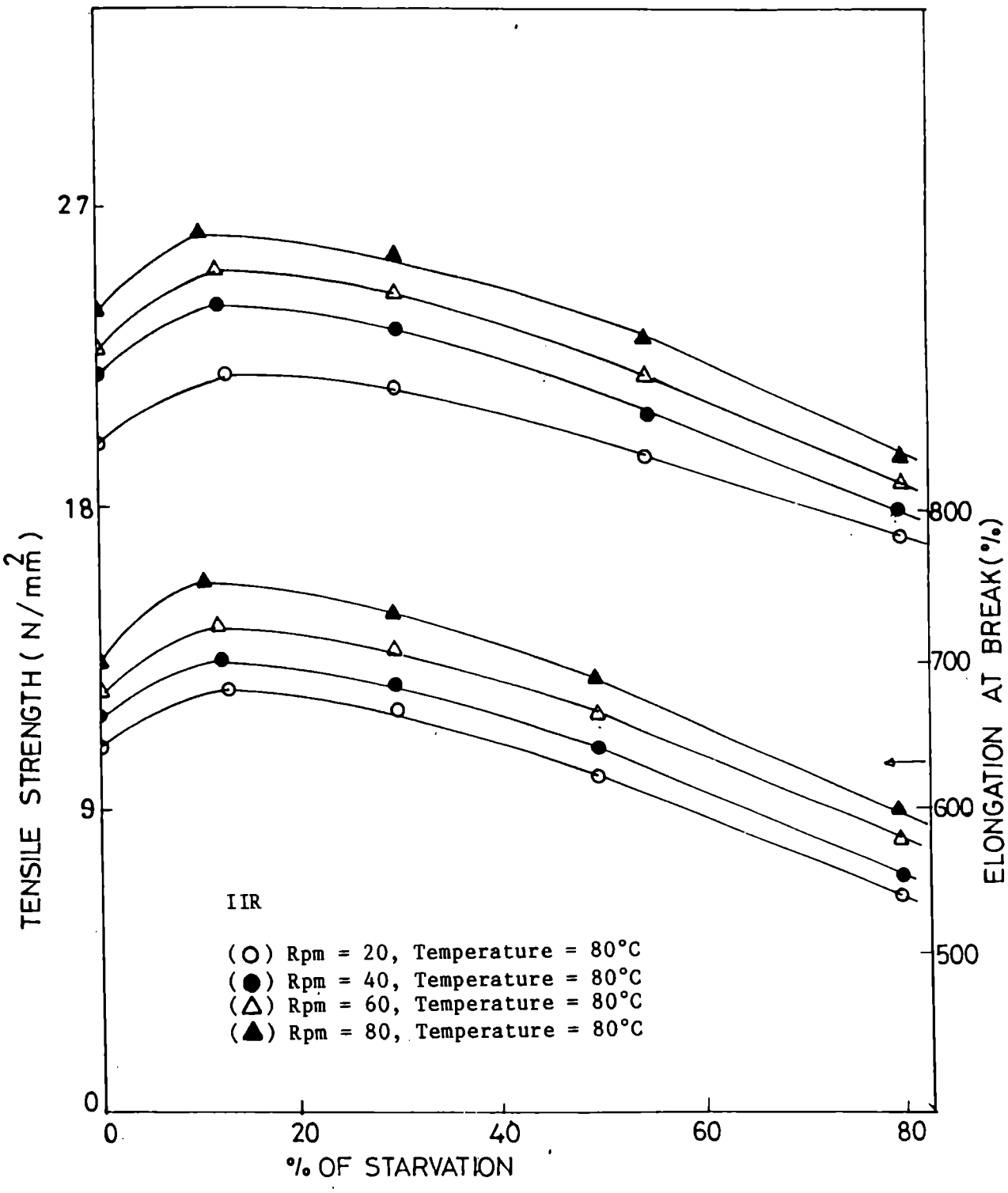


Fig.4.18: Variation of tensile strength and elongation at break of filled IIR vulcanizates with percentage starvation at different rpms.

rpms and at a constant temperature of 80°C. It is found that maximum properties are obtained at percentage starvations of 13, 12.5, 12 and 11 respectively at rpm of 20, 40, 60 and 80. The effect of percentage of starvation on the tensile properties of vulcanizates of filled IIR extruded compounds at different temperatures and at rpm of 40 is represented in the Fig.4.19. The percentages of starvation at which maximum properties are observed are 14, 12.5, 11 and 10 respectively at temperatures of 60°C, 80°C, 100°C and 120°C.

Tables 4.3a and 4.3b represent the variation of other physical properties like tear strength, hardness, and compression set with percentage of starvation. Generally it can be concluded that the maximum properties of the extrudates are observed at low percentages of starvation. Moreover, percentage of starvation at which maximum properties are observed decreases either with increase in rpm or increase in temperature of extrusion.

4.3.4 Extrusion variables

Quality of the extrudates depends on the fluctuations of main extrusion variables, that is, temperature, pressure and flow rate.[13-15] Their fluctuations are not independent of one another. But the most independent factor is temperature fluctuation and so its amplitude has been considered as one of the important criteria of screw performance

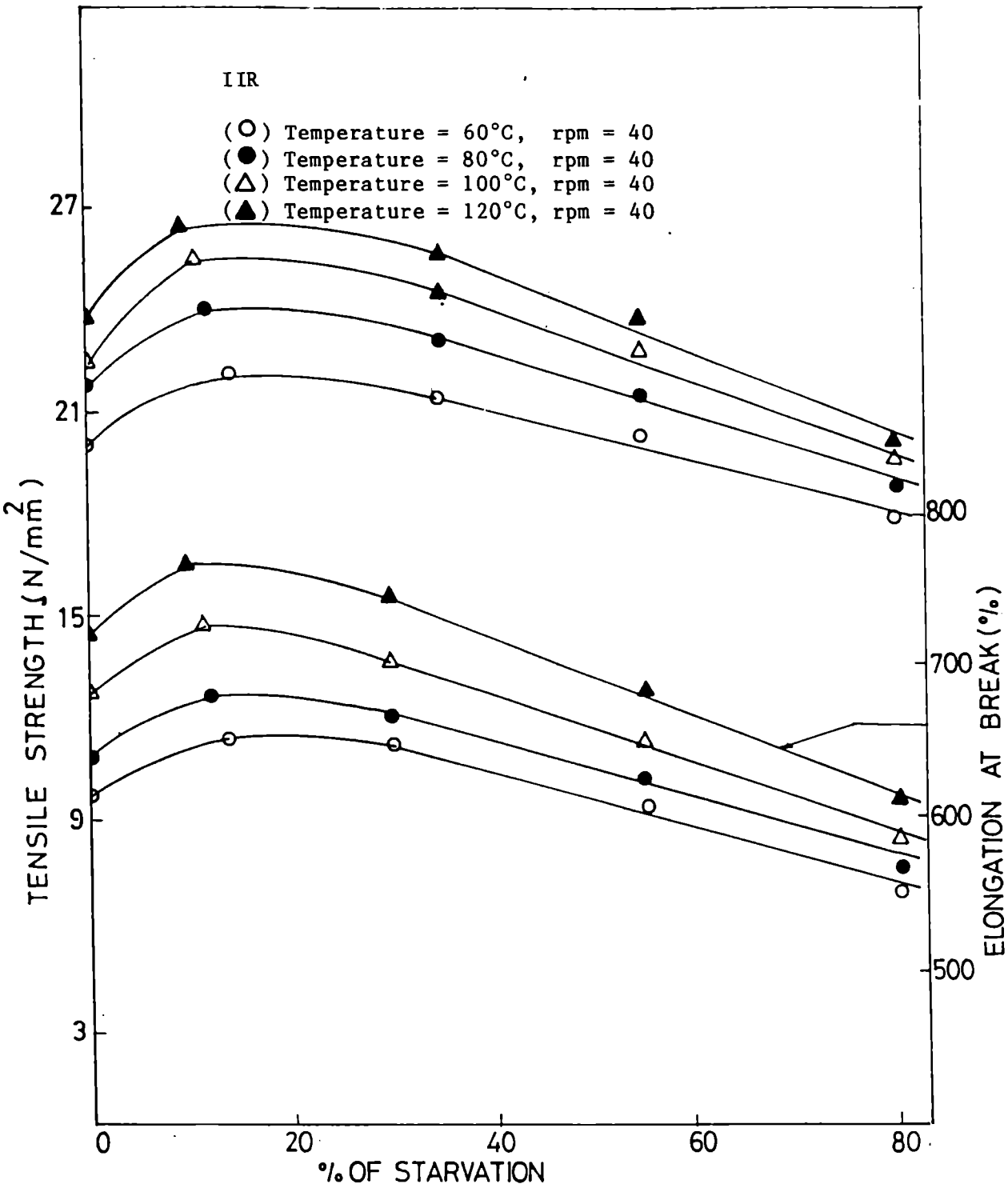


Fig.4.19: Variation of tensile strength and elongation at break of filled IIR vulcanizates with percentage starvation at different temperatures.

Table 4.3a: Variation of physical properties of NR, SBR and IIR filled vulcanizates with percentage of starvation

% Starvation	NR Extruded at rpm 40; Temp. 90°C			SBR Extruded at rpm 40; Temp. 100°C			IIR Extruded at rpm 40; Temp. 120°C		
	Tear strength (N/mm)	Hardness (Shore A)	Compress-ion set (%)	Tear strength (N/mm)	Hardness (Shore A)	Compress-ion set (%)	Tear strength (N/mm)	Hardness (Shore A)	Compress-ion set (%)
80	82.41	41	38.81	48.91	51	45.20	43.14	47	49.24
50	85.58	46	36.94	51.88	55	43.81	47.81	51	47.58
30	89.87	50	34.41	55.45	59	41.44	49.96	54	45.36
10	95.99	52	33.28	61.13	62	40.22	54.77	57	44.09
0 (Flood feeding)	88.74	49	36.30	57.25	60	42.35	47.51	54	46.87
Force feeding	84.31	46	39.45	52.81	56	44.94	44.46	52	48.90

Table 4.3b: Variation of physical properties of NR, SBR and IIR filled vulcanizates with percentage of starvation

% Starvation	NR Extruded at rpm 80 Temp. 80°C			SBR Extruded at rpm 80; Temp. 80°C			IIR Extruded at rpm 80; Temp. 80°C		
	Tear strength (N/mm)	Hardness (Shore A)	Compress-ion set (%)	Tear strength (N/mm)	Hardness (Shore A)	Compress-ion set (%)	Tear strength (N/mm)	Hardness (Shore A)	Compress-ion set (%)
80	85.62	46	35.81	50.35	55	41.34	45.71	51	46.24
50	88.38	50	33.94	54.84	60	39.23	50.38	56	44.81
30	95.84	53	30.10	62.97	63	37.80	54.56	59	42.38
10	99.01	56	29.05	68.99	66	35.71	59.94	62	41.13
0 (Flood feeding)	94.11	52	33.41	62.40	62	38.45	52.24	58	43.22
Force feeding	90.07	50	35.62	57.28	60	40.21	47.80	55	47.70

evaluation and hence the extrudate quality.[16] Properties of polymers depend less on pressure than on temperature.[13]

Tables 4.4, 4.5 and 4.6 represent the fluctuations of die temperature and flow rate in the extrusion of NR, SBR and IIR filled compounds. The fluctuations in temperature and flow rate which are prominent at the flood feeding (zero starvation), force feeding and at the higher levels of starvation. The fluctuations are comparatively low at the lower levels of starvation (mainly at 10% starvation). The variation in temperature and flow rate is in conformation with the observation that the die pressure fluctuations get reduced at low levels of starvation of 10 to 25%.[3,17,18]

A high quality in the operation of a screw signifies an extrusion with minimum temperature, pressure and flow rate fluctuations at a temperature that does not exceed polymer resistance to thermal degradation[15] at low levels of starvation.

4.3.5 Ageing studies

Figures 4.20 and 4.21 show the variation of tensile strength and elongation at break before and after ageing for the filled vulcanizates of extruded NR, SBR and IIR compounds. It is observed that maximum retention in properties is observed at the low level of starvation at which maximum properties are observed for NR, SBR and IIR vulcanizates.

Table 4.4: Fluctuations of temperature and flow rate in the extrusion of NR filled compounds at 1 min. intervals

Rpm	% Starvation	Temperature (°C)		Flow rate (mg/min)
		Set	Actual	
80	80	80	79 81 80 82 80	6500 7650 6800 8109 7205
80	50	80	79 80 82 81 80	17250 18510 19255 18675 17900
80	30	80	80 81 80 81 79	25200 26410 25225 25910 24811
80	I0	80	80 80 79 79 80	32801 32752 31412 31600 32200
80	0 (Flood feeding)	80	80 79 78 79 8I	36201 35900 34820 35701 36650
80	Force feeding	80	78 80 81 79 78	38501 39540 40000 3900I 38293

Table 4.5 Fluctuations of temperature and flow rate in the extrusion of SBR filled compounds at 1 min. intervals

Rpm	% starvation	Temperature (°C)		Flow rate (mg/min)
		Set	Actual	
60	80	80	79	5890
			78	4995
			80	6215
			79	5500
			78	4510
60	50	80	79	13590
			78	12840
			80	14355
			79	13001
			80	13815
60	30	80	80	20010
			79	19640
			79	19015
			80	20249
			79	19189
60	10	80	80	25900
			80	25585
			79	24680
			79	24305
			80	25295
60	0 (Flood feeding)	80	80	28001
			79	27395
			78	26845
			80	28390
			79	27500
60	Force feeding	80	78	28400
			79	29515
			78	28910
			80	30815
			81	31200

Table 4.6 Fluctuations of temperature and flow rate in the extrusion of IIR filled compounds at 1 min. intervals

Rpm	% starvation	Temperature (°C)		Flow rate (mg/min)
		Set	Actual	
40	80	100	100	4200
			99	3495
			98	2995
			99	3700
			100	4520
40	50	100	101	10100
			99	8545
			100	9500
			99	9002
			100	9399
40	30	100	100	12650
			101	13535
			100	13010
			99	12100
			100	12805
40	10	100	100	16800
			100	16450
			99	15803
			100	16515
			100	16020
40	0 (Flood feeding)	100	101	19050
			100	18545
			99	17840
			100	18100
			101	18800
40	Force feeding	100	101	20850
			99	19700
			98	18410
			99	19499
			100	20385

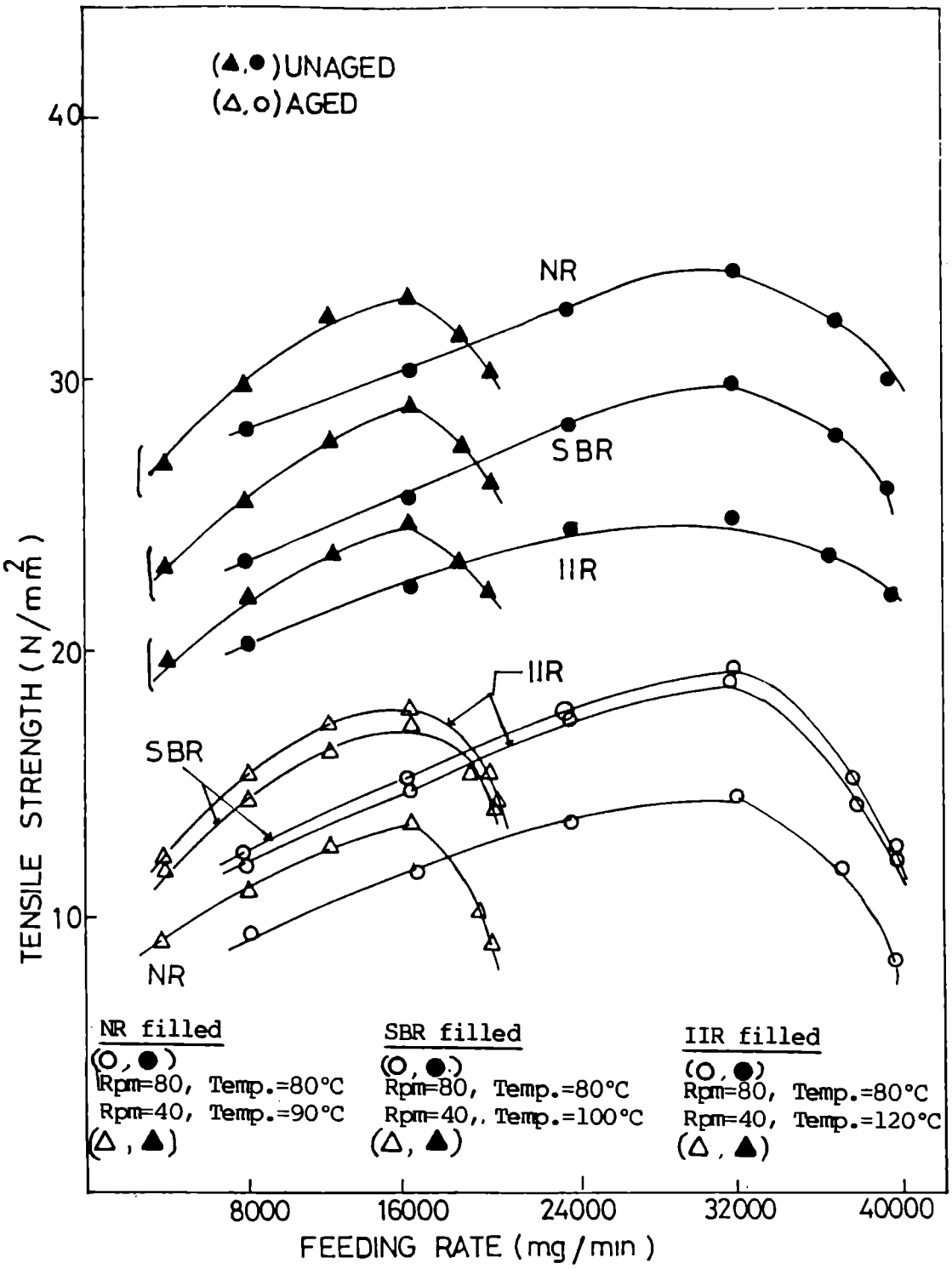


Fig.4.20: Variation of tensile strength of filled NR, SBR and IIR vulcanizates with feeding rate at different rpms and temperatures.

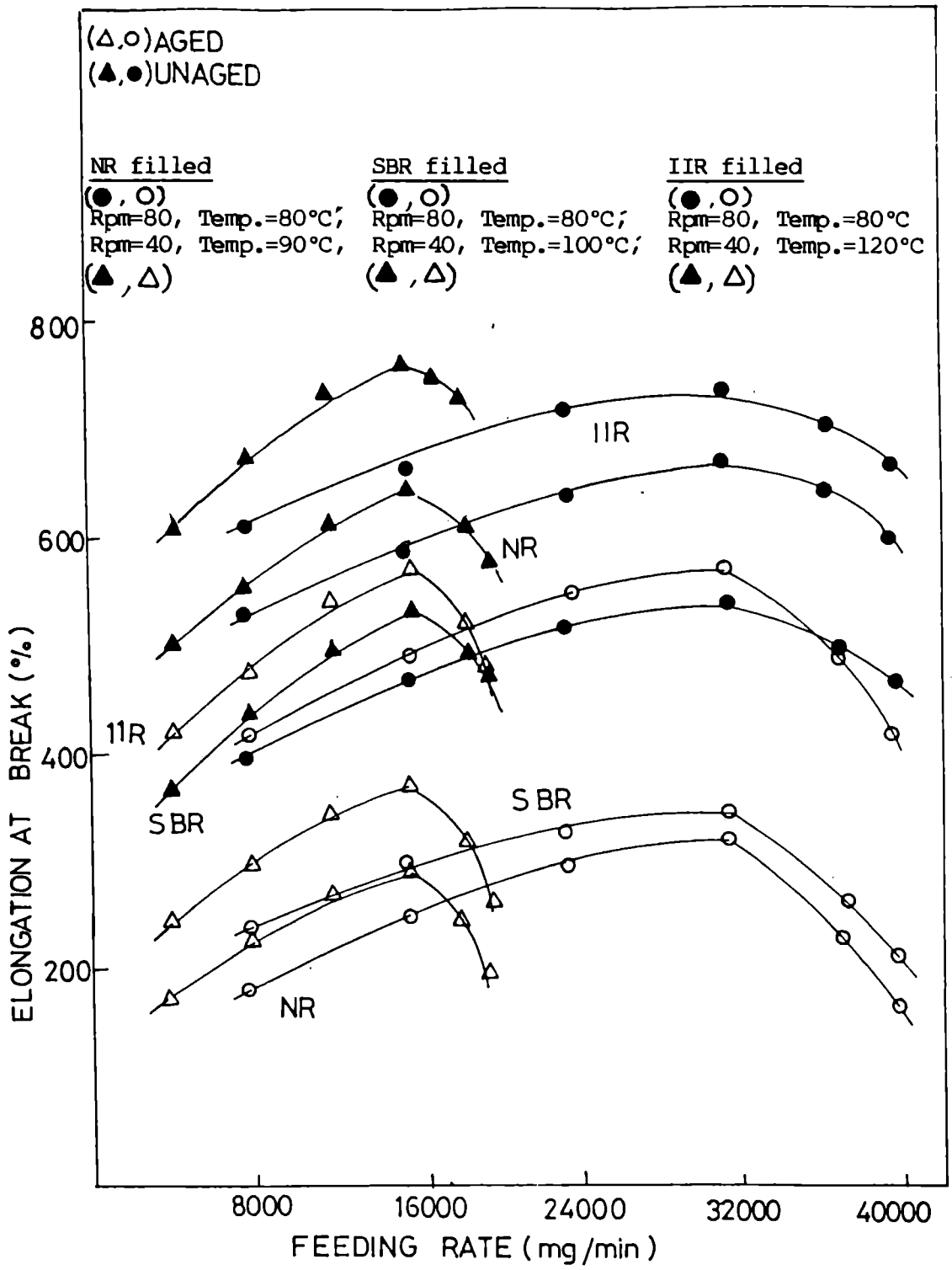


Fig.4.21: Variation of elongation at break of filled NR, SBR and IIR vulcanizates with feeding rate at different rpms and temperatures.

This again shows the thermal and shear uniformity of the compounds at this particular low level of starvation.

The values of tensile properties of filled vulcanizates of NR, SBR and IIR extruded compounds, before and after ageing at various levels of feeding with percentage retention are shown in Tables 4.7, 4.8 and 4.9 respectively. Figures 4.22–4.24 show the bar charts of the tensile properties of the extruded vulcanizates at an rpm of 80 and at a temperature of 80°C at the starve feeding, flood feeding and force feeding levels. During ageing the tensile strength and elongation at break are found to deteriorate more in the case of NR vulcanizates than those of SBR and IIR vulcanizates. This might be due to the significant conversion of polysulphidic crosslinks to di- and mono-sulphidic crosslinks and due to the main chain scission during ageing of NR.[19,20] But in the case of SBR and IIR extruded vulcanizates the main chain is more resistant to thermal breakdown and the small decrease in properties may be only due to the corresponding significant conversion of polysulphidic linkages to di- and mono-sulphidic linkages.[21]

4.3.6 Thermogravimetric analysis

TGA traces of starve fed, flood fed, and force fed samples of extruded NR vulcanizates are shown in the Figs.4.25–4.27 respectively. TGA traces of starve fed, flood fed and force fed samples of extruded SBR vulcanizates are shown in the Figs. 4.28–4.30 respectively and TGA

Table 4.7: Tensile properties of filled NR vulcanizates at different rpms and temperatures

% Starvation	NR compounds extruded at rpm 40; Temperature 90°C						NR compounds extruded at rpm 80; Temperature 80°C					
	Tensile strength (MPa)			Elongation at break (%)			Tensile strength (MPa)			Elongation at break (%)		
	Before ageing	After ageing	Retention %	Before ageing	After ageing	Retention %	Before ageing	After ageing	Retention %	Before ageing	After ageing	Retention %
80	27.45	9.01	32.8	503	171	34.0	28.53	9.51	33.3	528	182	34.4
50	30.48	11.01	36.1	557	225	40.4	30.62	11.89	38.8	592	254	42.9
30	32.20	12.81	39.8	616	274	44.5	32.68	13.54	41.4	642	327	50.9
10	33.19	13.50	40.7	642	302	47.0	34.1	14.59	42.8	671	348	51.9
0 (Flood feeding)	32.50	12.18	37.5	612	255	41.7	32.80	13.12	40.0	638	282	44.2
Force feeding	30.16	9.28	30.8	575	198	34.4	30.01	9.54	31.8	594	162	27.3

Table 4.8: Tensile properties of filled SBR vulcanizates at different rpms and temperatures

% Starvation	SBR compounds extruded at rpm 40: Temperature 100°C						SBR compounds extruded at rpm 80; Temperature 80°C					
	Tensile strength (MPa)			Elongation at break (%)			Tensile strength (MPa)			Elongation at break (%)		
	Before ageing	After ageing	Retention %	Before ageing	After ageing	Retention %	Before ageing	After ageing	Retention %	Before ageing	After ageing	Retention %
80	23.02	11.41	49.5	372	248	66.7	23.40	12.35	52.8	401	235	58.6
50	25.44	14.42	56.7	438	289	66	25.61	15.56	60.8	470	287	61.1
30	26.77	16.02	59.8	501	340	67.9	28.58	18.23	63.8	519	331	63.8
10	29.01	17.82	61.4	536	371	69.0	30.20	19.66	65.1	543	348	64.1
0 (Flood feeding)	27.82	16.11	57.9	520	318	61.2	28.84	16.40	56.9	515	282	54.8
Force feeding	26.42	13.34	50.5	490	265	54.1	25.92	12.61	48.6	468	212	45.3

Table 4.9: Tensile properties of filled IIR vulcanizates at different rpms and temperatures

% Starvation	IIR compounds extruded at rpm 40; Temperature 120°C						IIR compounds extruded at rpm 80; Temperature 80°C					
	Tensile strength (MPa)			Elongation at break (%)			Tensile strength (MPa)			Elongation at break (%)		
	Before ageing	After ageing	Retention %	Before ageing	After ageing	Retention %	Before ageing	After ageing	Retention %	Before ageing	After ageing	Retention %
80	19.60	12.10	61.7	607	422	69.5	20.14	11.95	59.3	622	418	67.2
50	21.77	15.20	69.8	677	481	71.0	22.34	14.81	66.3	670	488	72.8
30	23.54	17.12	72.7	738	550	74.5	24.57	17.42	70.09	721	551	76.4
10	24.58	18.02	73.5	762	581	76.2	25.20	18.93	75.1	738	579	78.5
0 (Flood feeding)	23.49	16.41	69.9	728	488	67.0	23.94	16.30	68.1	707	517	73.1
Force feeding	22.61	14.31	64.2	682	440	64.5	22.24	12.20	54.9	672	410	61.0

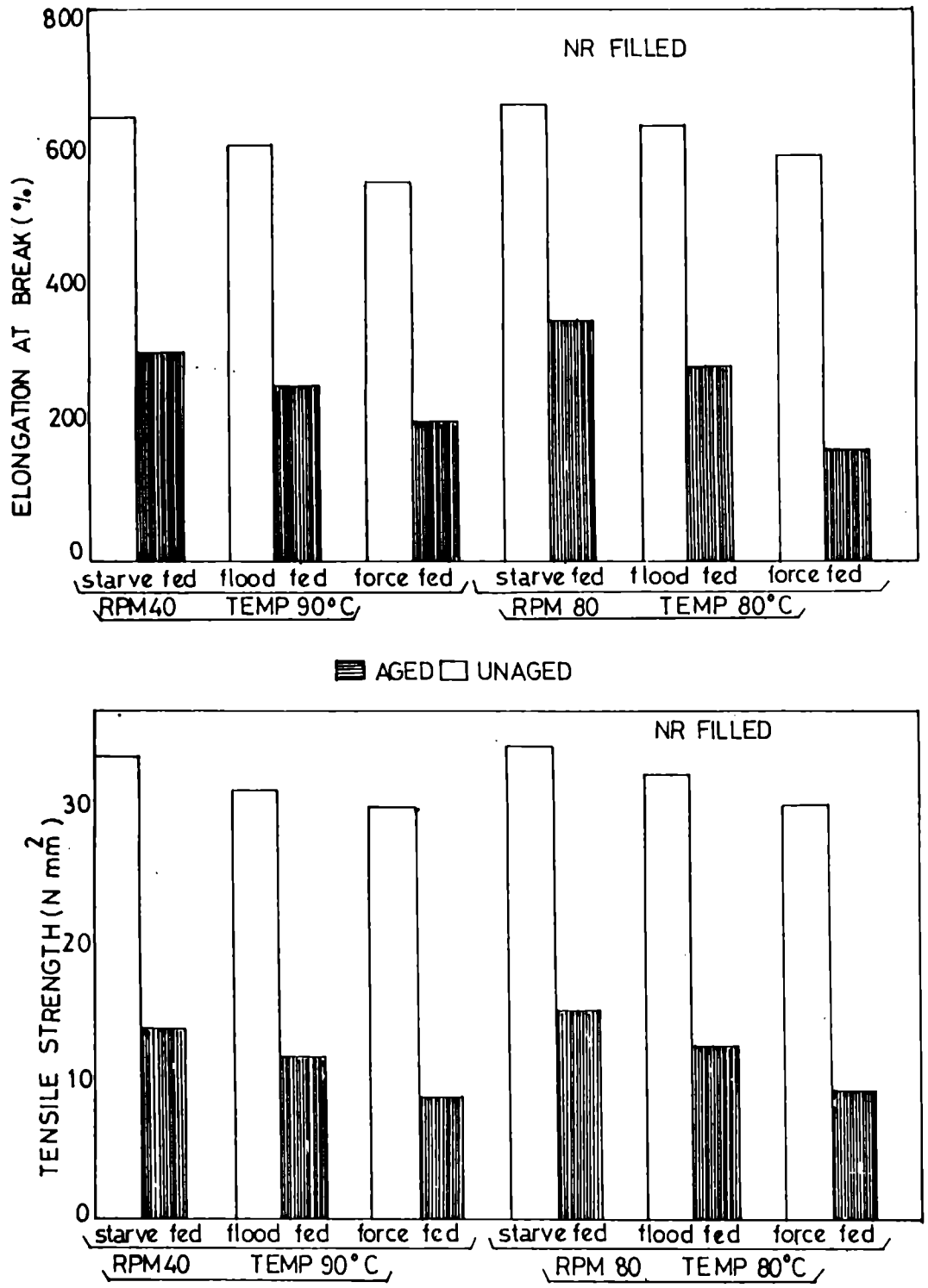
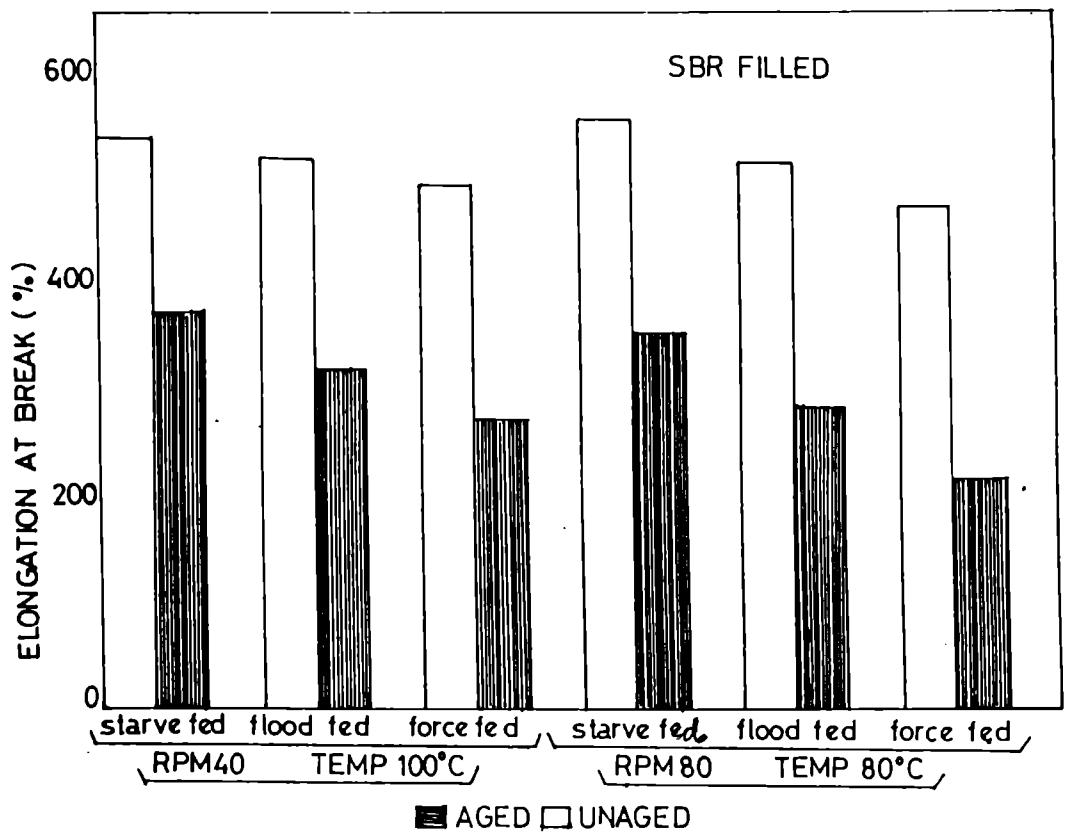


Fig.4.22: Variation of tensile strength and elongation at break of filled NR vulcanizates with different levels of feeding at different rpms and temperatures.



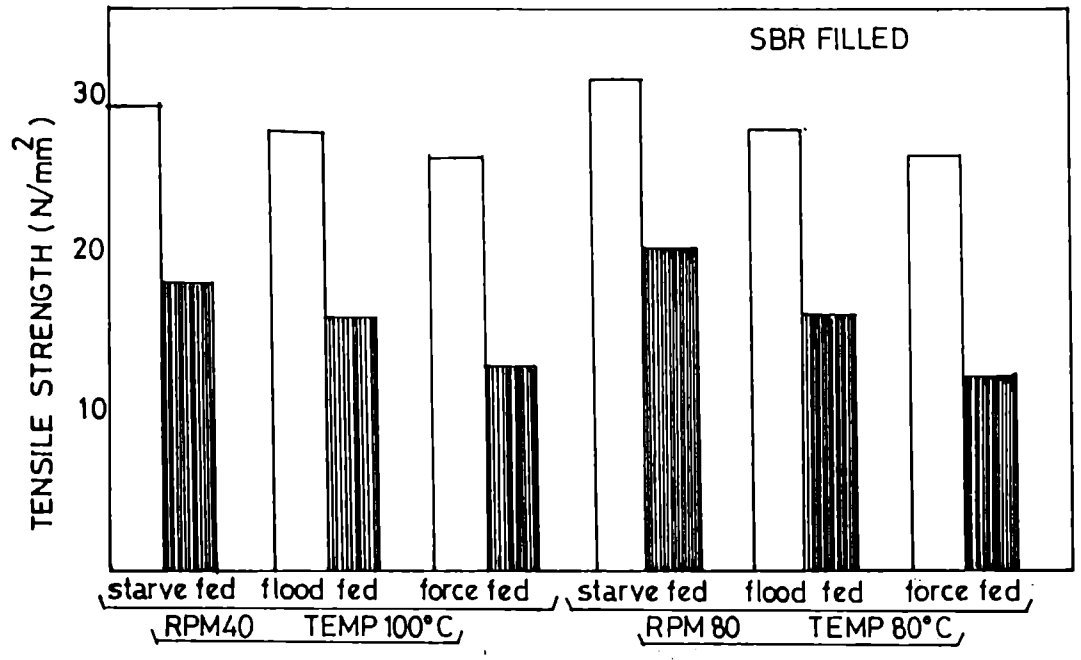


Fig.4.23: Variation of tensile strength and elongation at break of filled SBR vulcanizates with different levels of feeding at different rpms and temperatures.

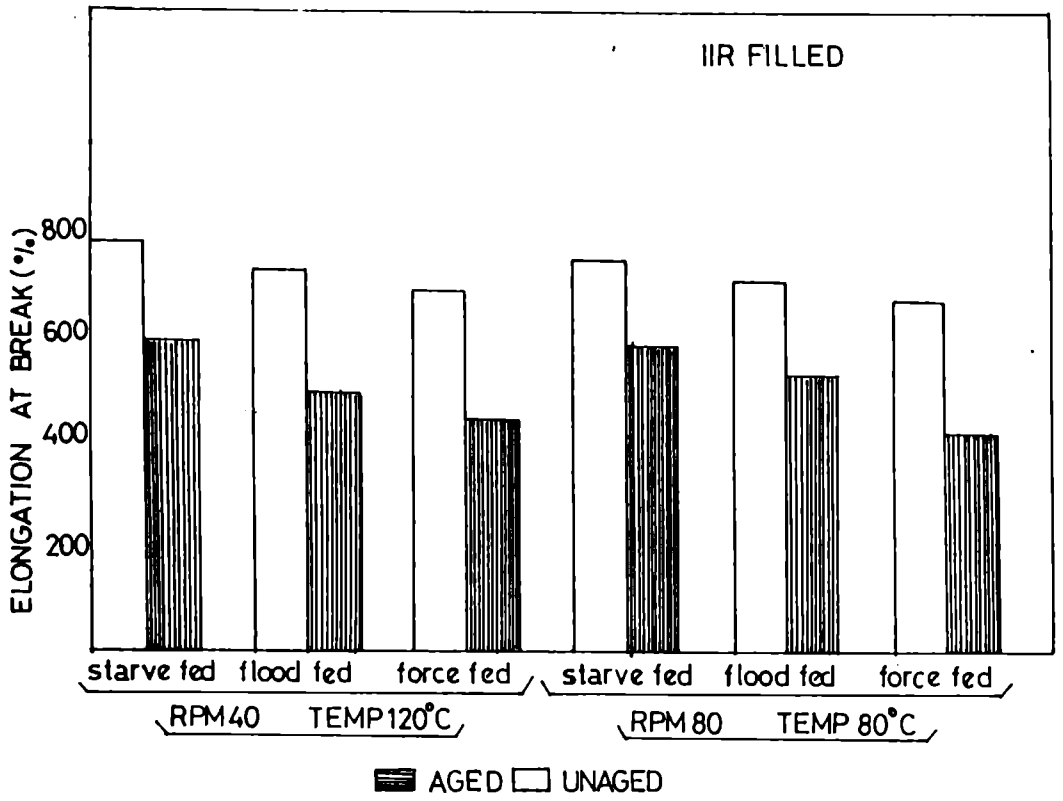


Fig.4.24: Variation of tensile strength and elongation at break of filled IIR vulcanizates with different levels of feeding at different rpms and temperatures.

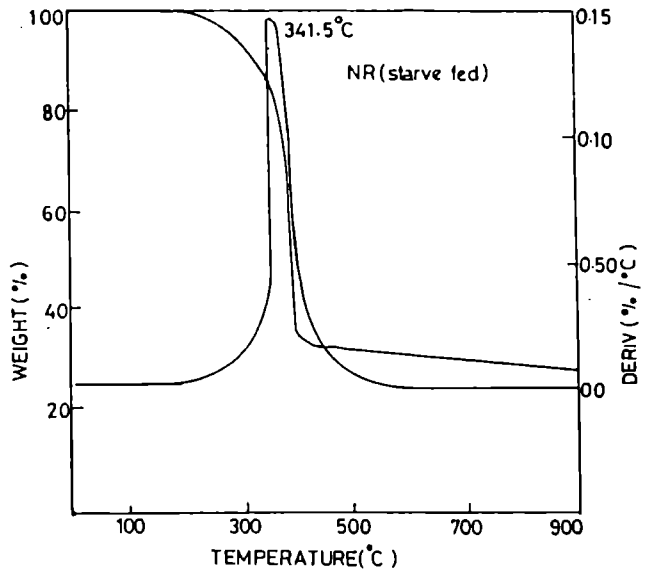


Fig.4.25
Starve fed

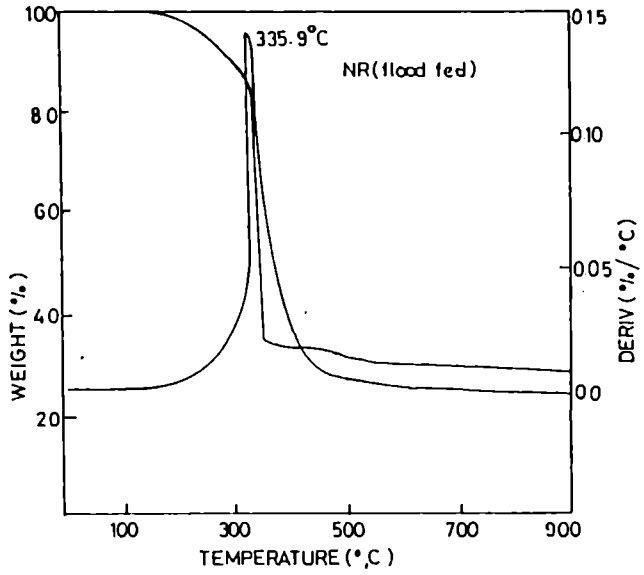


Fig.4.26
Flood fed

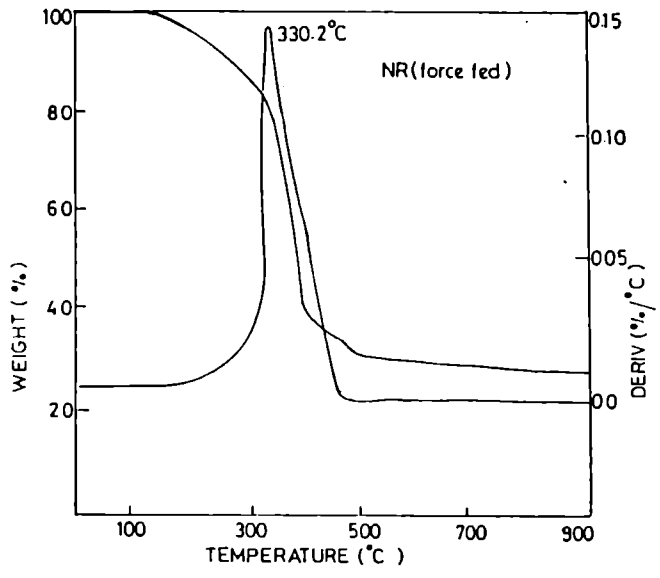


Fig.4.27
Force fed

TGA traces of filled vulcanizates of NR compounds.

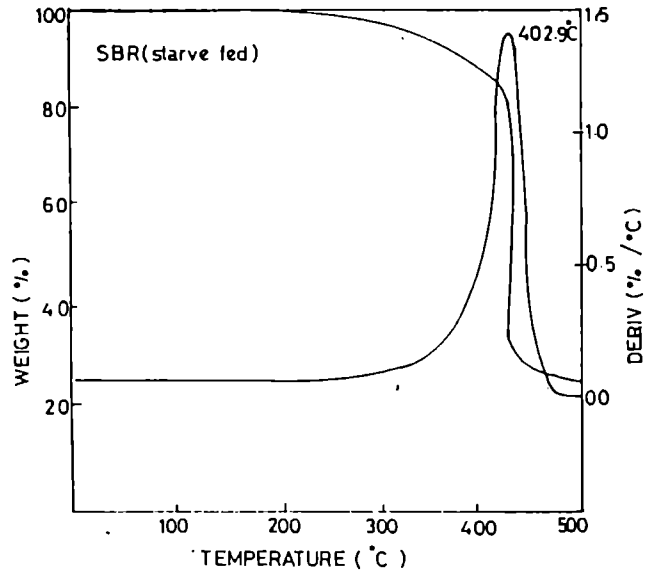


Fig.28
Starve fed

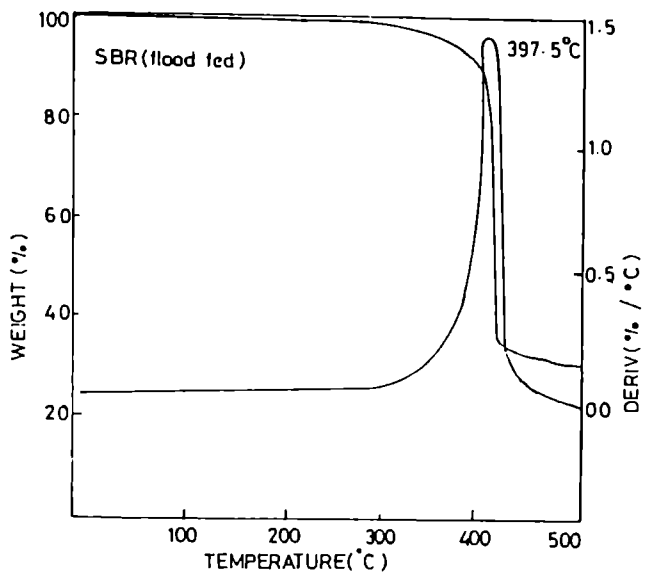


Fig.4.29
Flood fed

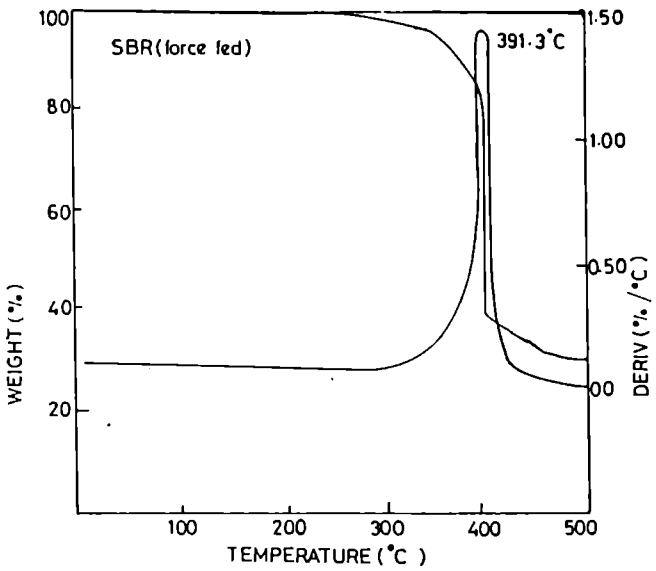


Fig.4.30
Force fed

TGA traces of filled vulcanizates of SBR compounds.

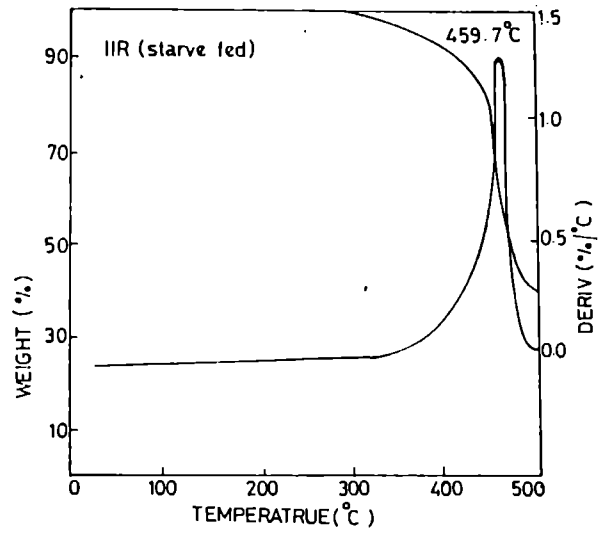


Fig.4.31
Starve fed

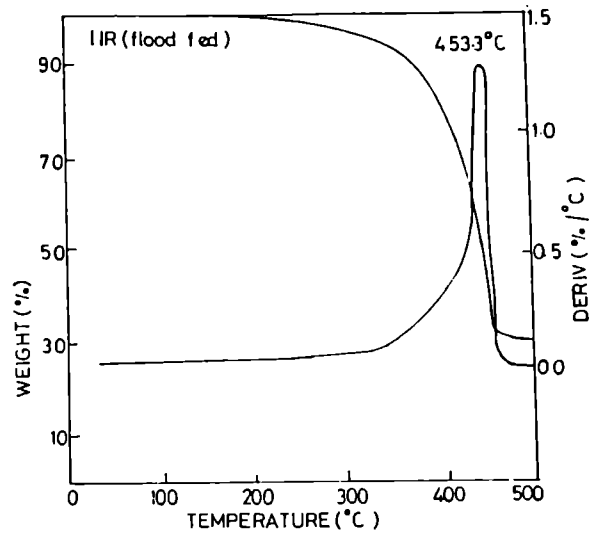


Fig.4.32
Flood fed

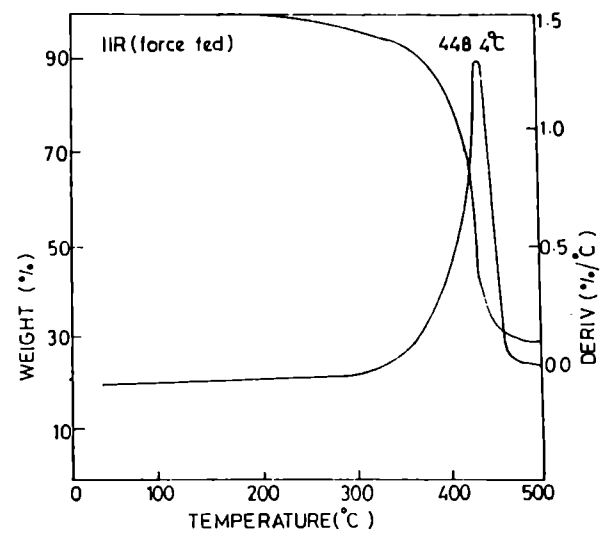


Fig.4.33
Force fed

TGA traces of filled vulcanizates of IIR compounds.

traces of the corresponding samples of extruded IIR vulcanizates are shown in the Figs. 4.31–4.33 respectively. It is found that the starve fed sample (at low level of starvation) has higher transition temperature than the flood fed and force fed samples. This further shows that starve fed compound is more thermally stable than the flood fed or the force fed sample, which clearly results from the more uniform temperature and shear history to which the compound was subjected to in starved extrusion than the normal/forced extrusion. It is noticed that the flood fed sample has higher transition temperature than the force fed sample. This indicates the higher thermal stability of the flood fed sample than that of the force fed sample.

4.3.7 Density and viscosity.

Table 4.10 shows the variation of density of a selected number of samples of filled vulcanizates of NR, SBR and IIR. When the percentage of starvation increases, it is observed that there is a marginal decrease in the densities of the vulcanizates. Density of the NR sample at the low level of starvation is more or less the same as that of the flood fed sample, while the density of the samples of SBR and IIR vulcanizates at the low levels of starvation is marginally less than that of the corresponding flood fed samples.

The variation of Brookfield viscosity values of solutions of a few samples of NR, SBR and IIR extruded compounds is also shown in the

Table 4.10: Variation of density, Brookfield viscosity, swelling index, total crosslink density and bound rubber content of filled NR, SBR and IIR compounds with percentage of starvation

	Feeding rate (mg/min)	Percentage starvation	Density (g/cc)	Viscosity (centipoise)	Swelling index	Total crosslink density x 10^5 g mol/cm^3	Bound rubber content %
NR extruded at 80 rpm and 80°C	7200	80	1.1175	203400	2.52	3.92	28
	18000	50	1.1182	205200	2.38	4.85	33
	25200	30	1.1214	207000	2.16	5.36	39
	32400	10	1.1246	208000	2.09	7.13	48
	36000	0 (Flood feeding)	1.1248	207200	2.25	4.91	36
	40000	Force feeding	1.1244	204800	2.33	4.58	30
SBR extruded at 80 rpm and 80°C	7200	80	1.1471	42100	2.56	4.31	31
	18000	50	1.1495	43200	2.03	5.28	36
	25200	30	1.1538	44700	1.74	7.41	45
	32400	10	1.1582	45900	1.24	9.93	54
	36000	0 (Flood feeding)	1.1616	44500	1.80	6.01	41
	40000	Force feeding	1.1587	42700	1.91	4.92	33
IIR extruded at 40 rpm and 120°C	3600	80	1.1268	19420	1.62	7.16	36
	9000	50	1.1285	19900	1.50	8.50	39
	12600	30	1.1322	20540	1.36	9.01	46
	16200	10	1.1375	21420	1.20	10.16	57
	18000	0 (Flood feeding)	1.1392	20100	1.39	8.23	45
	20000	Force feeding	1.1376	19640	1.43	6.52	41

table 4.10. It is found that the viscosity of the solutions of NR, SBR and IIR extruded compounds increase with feeding rate, reach a maximum value in the starved region, as in the case of the variation of physical properties. The maximum value of viscosity is observed at the low level of starvation at which maximum properties were observed. Since viscosity is a measure of average molecular weight[22,23], it can be concluded that starved extrusion leads to lower mechanical breakdown.

4.3.8 Swelling index and crosslink density

The most important characteristic of an elastomeric network is unquestionably its degree of crosslinking.[10,24] This aspect of network structure affects most of the elastomeric properties.[9,11]

The variation in swelling index and crosslink density (1/2Mc) of the samples of filled vulcanizates of extruded NR, SBR and IIR compounds is shown in the table 4.10. It is found that samples which give maximum physical properties exhibit the least swelling index and maximum crosslink density.[9,12]

4.3.9 Percentage bound rubber content

Table 4.10 also shows the variation of percentage bound rubber[25] content of the vulcanizates of filled extruded NR, SBR and IIR compounds. It is found that the maximum percentage bound rubber content is observed in the extruded vulcanizates at the low levels of

starvation, at which maximum physical properties are observed. This behaviour is expected since bound rubber has long been recognised as an important factor in the proper rubber–filler interaction and hence in rubber properties.[26,27]

4.3.10 Dispersion studies

Figures 4.34–4.36 represent the photomicrographs of starve fed, flood fed and force fed samples of filled vulcanizates of NR extruded compounds respectively. It is observed that there is a marginal improvement in the filler dispersion in the starve fed (at low level of starvation) sample than that in the flood fed and force fed samples. Figures4. 37–4.39 represent the photomicrographs of starve fed, flood fed, and force fed samples of filled vulcanizates of SBR extruded compounds respectively and figures 4.40–4.42 represent the corresponding samples of filled vulcanizates of IIR extruded compounds respectively. In both cases of SBR and IIR it is noticed that carbon black dispersion is marginally better in the starve fed (at low level of starvation) sample than that in the flood fed and force fed samples.

4.3.11 SEM studies

SEM is widely employed to observe the microstructure of fracture surfaces and hence to study the fracture mechanisms of rubbers.[28-30] The tensile fracture surfaces of the starve fed, flood fed and force fed vulcanizates of filled NR extruded vulcanizates are shown in the

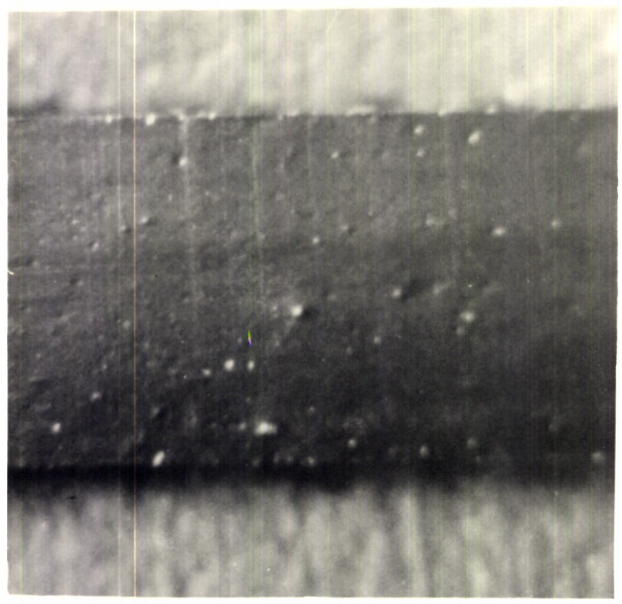


Fig.4.34 Starve fed

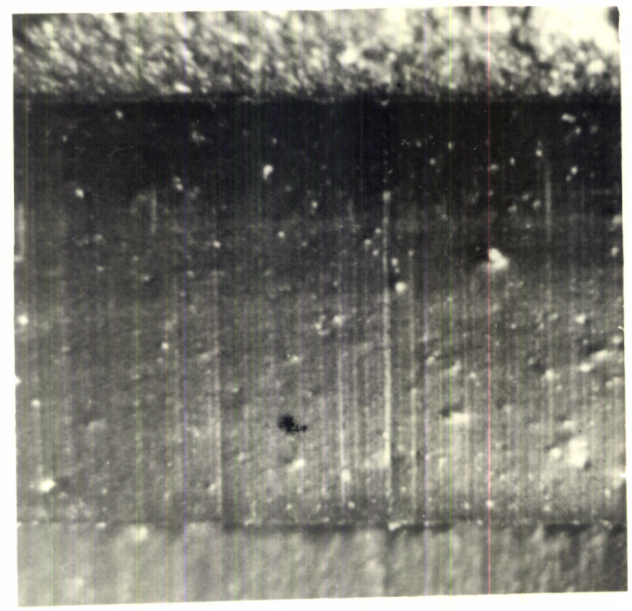


Fig.4.35 Flood fed

Fig.4.36 Force fed

Photomicrographs of NR filled vulcanizates.

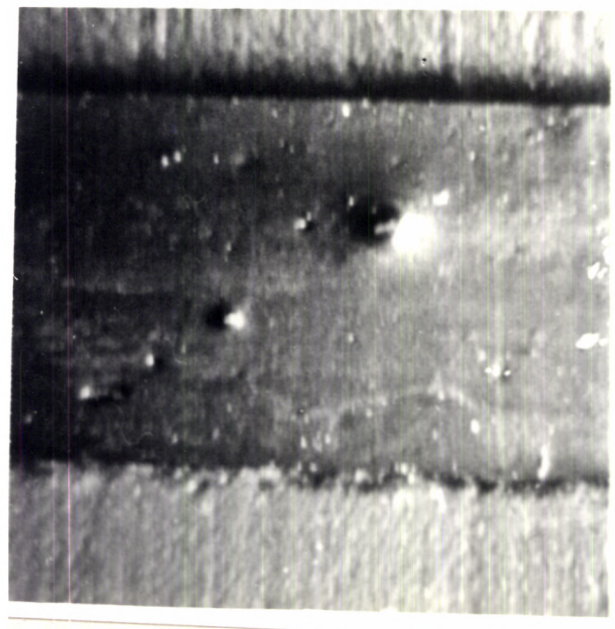


Fig.4.37 Starve fed

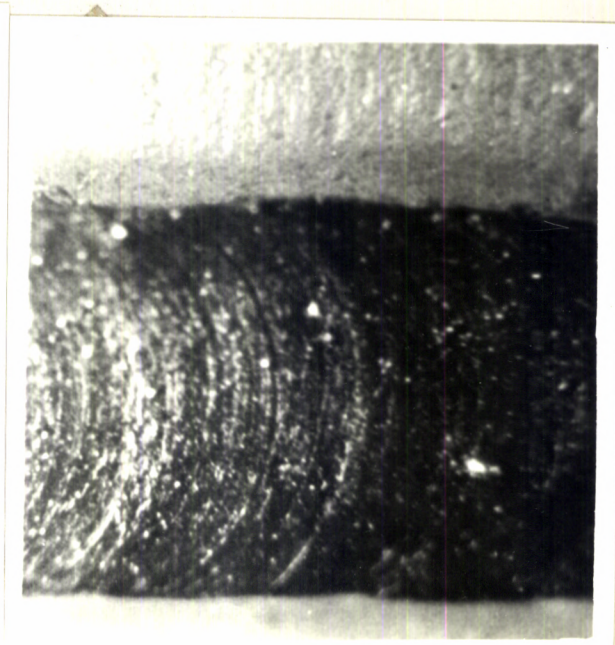


Fig.4.38 Flood fed

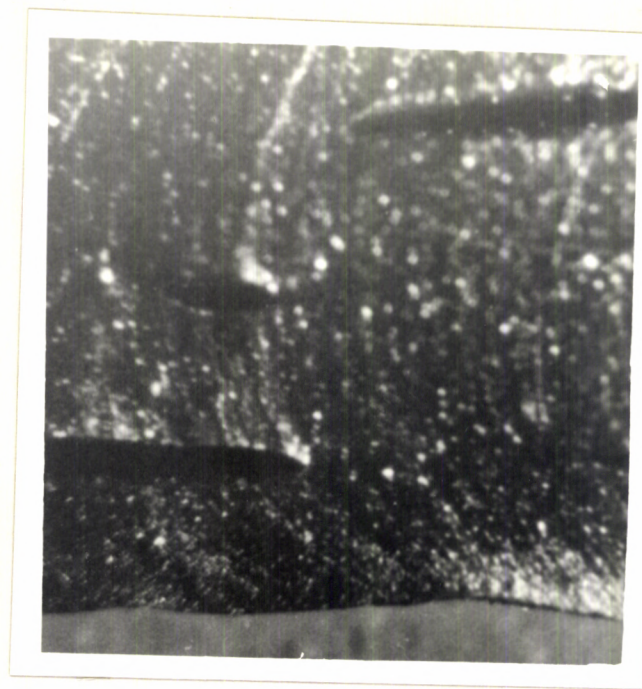


Fig.4.39 Force fed

Photomicrographs of SBR filled vulcanizates

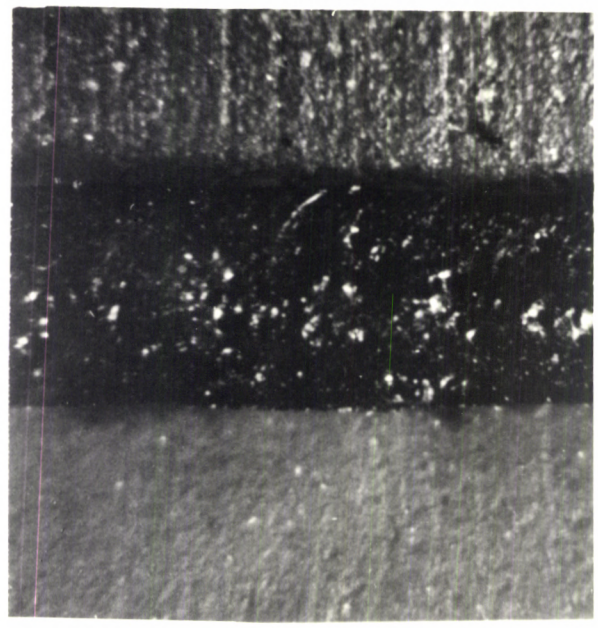


Fig.4.40 Starve fed

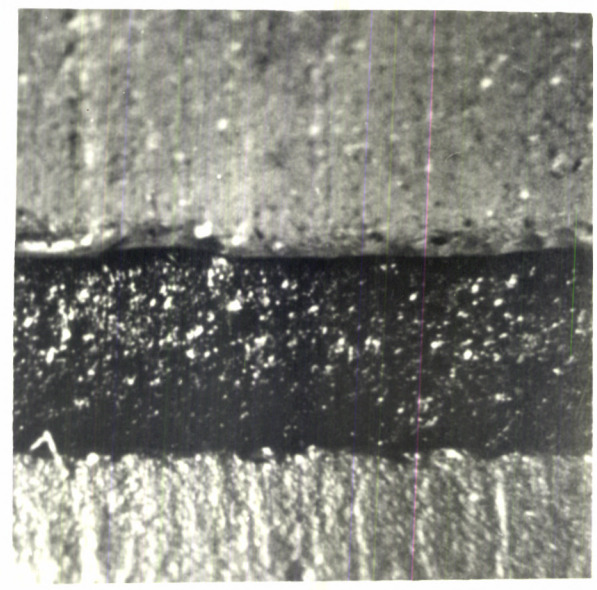


Fig.4.41 Flood fed

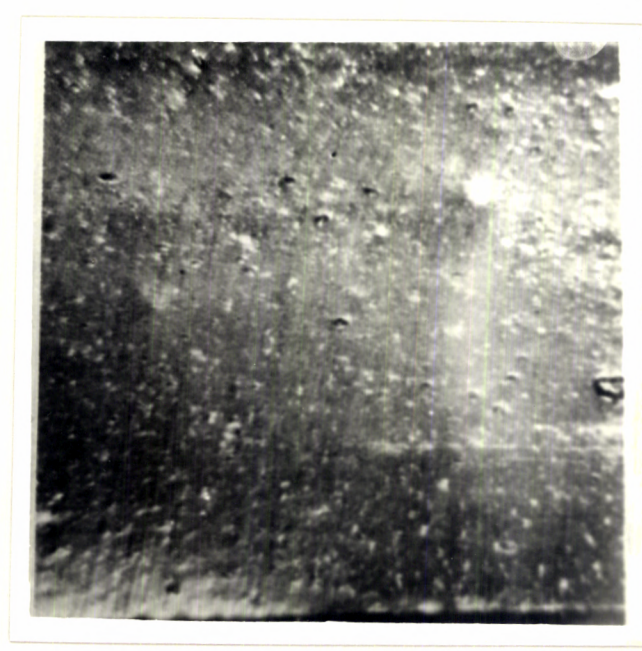


Fig.4.42 Force fed

Photomicrographs of IIR filled vulcanizates.

Figs.4.43–4.45 respectively. It is observed that the failure mechanism of the starve fed sample is different from that of the flood fed sample and force fed sample showing its superiority, obviously due to more uniform temperature distribution. The increase in crosslink density of the matrix of the starve fed sample, which results in enhanced strength[31] can be observed from the SEM photographs by the progressive increase in the roughness[28] of the fracture surfaces between Figs.4.43, 4.44 and 4.45. Moreover, there is a more regular pattern in the fracture surface of the starve fed sample which further indicates more uniform temperature distribution and shear history.

Figures 4. 46–4.48 show the tensile fracture surfaces of the starve fed, flood fed and force fed vulcanizates of filled SBR extruded compounds respectively. In the starve fed sample, the tear lines become uniformly broader with many branches[32] than that in the flood fed and force fed samples due to the higher crosslink density. Straight uniform broader tear lines in the starve fed sample also show the uniform temperature distribution and shear history of the compounds.

Figure 4.49–4.51 represent the tensile fracture surfaces of the starve fed, flood fed and force fed vulcanizates of filled IIR extruded vulcanizates respectively. The higher values of strength observed in the starve fed sample is reflected in the nature of the fracture surface also. In the starved sample, the surface is rough and the number of tear lines is

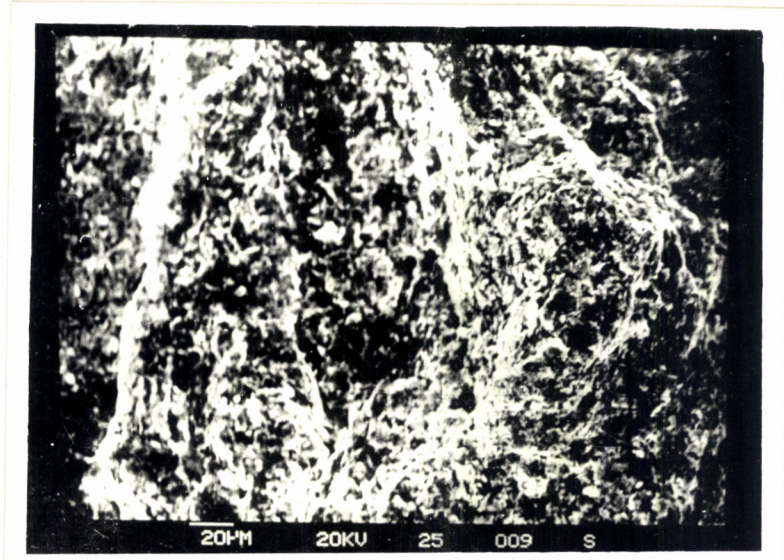


Fig.4.43 Starve fed

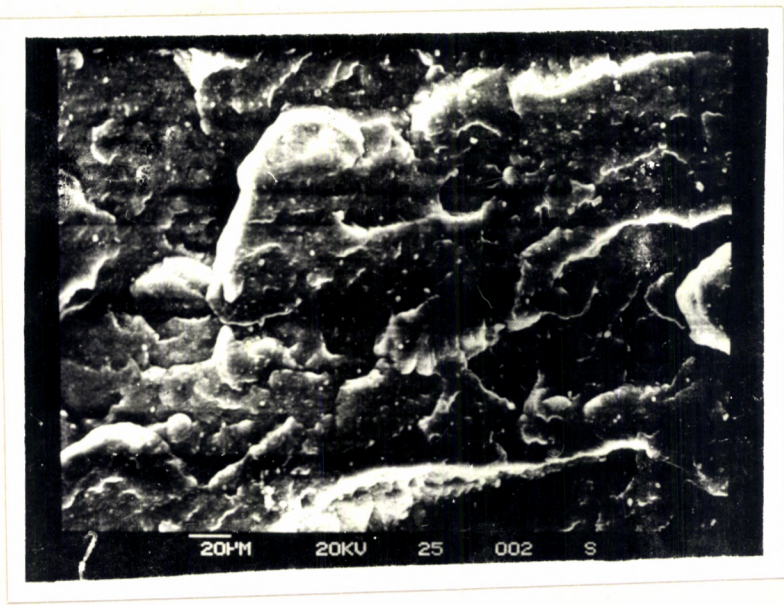


Fig.4.44 Flood fed

SEM photographs of the tensile fracture surfaces of the filled NR vulcanizates.

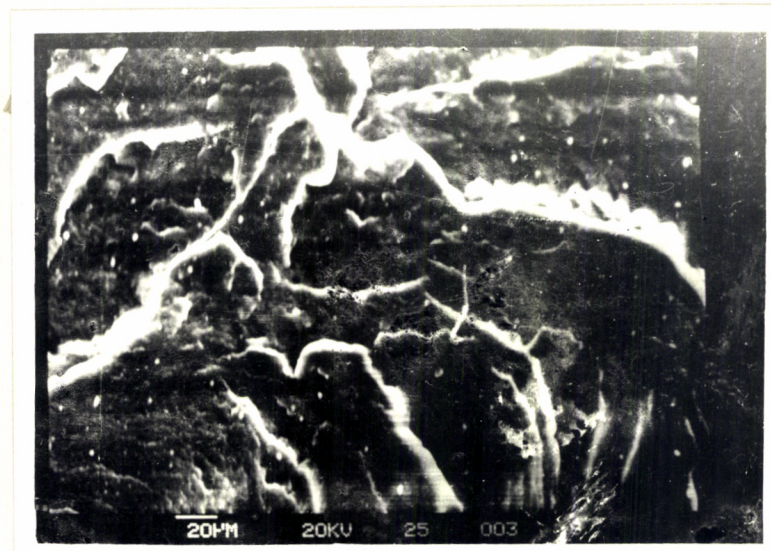


Fig.4.45 Force fed

SEM photograph of the tensile fracture surface of filled NR vulcanizate.

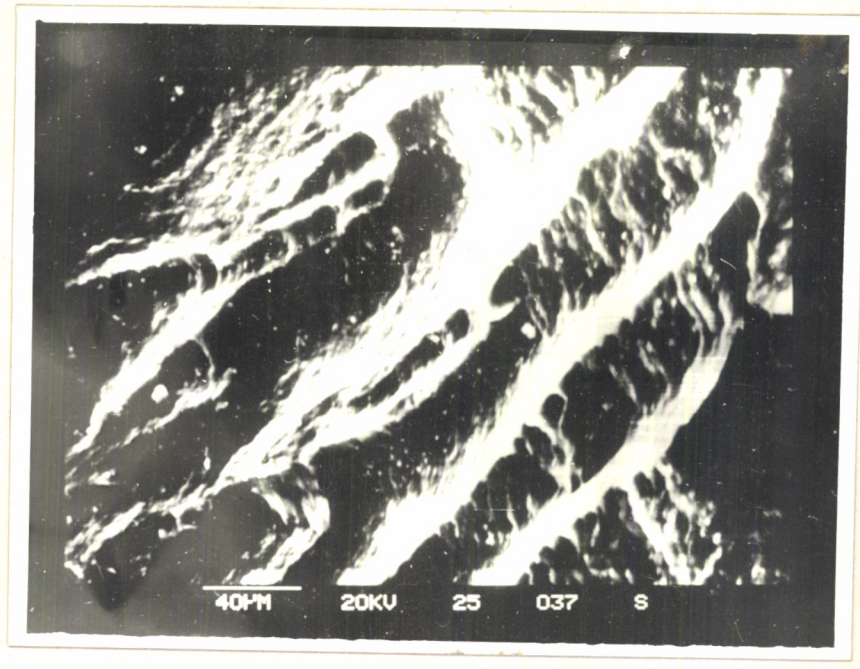


Fig.4.46 Starve fed

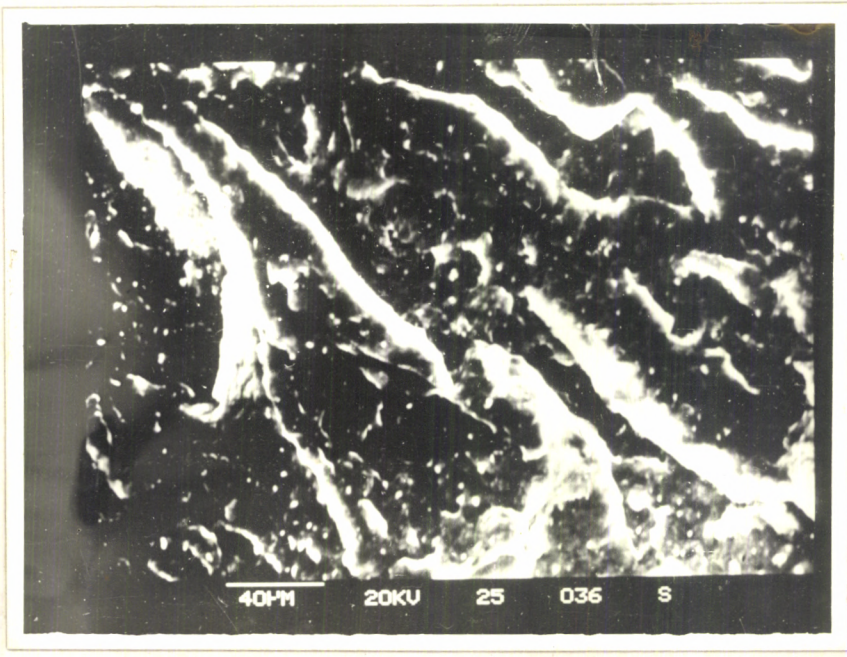


Fig.4.47 Flood fed

SEM photographs of the tensile fracture surfaces of SBR vulcanizates.

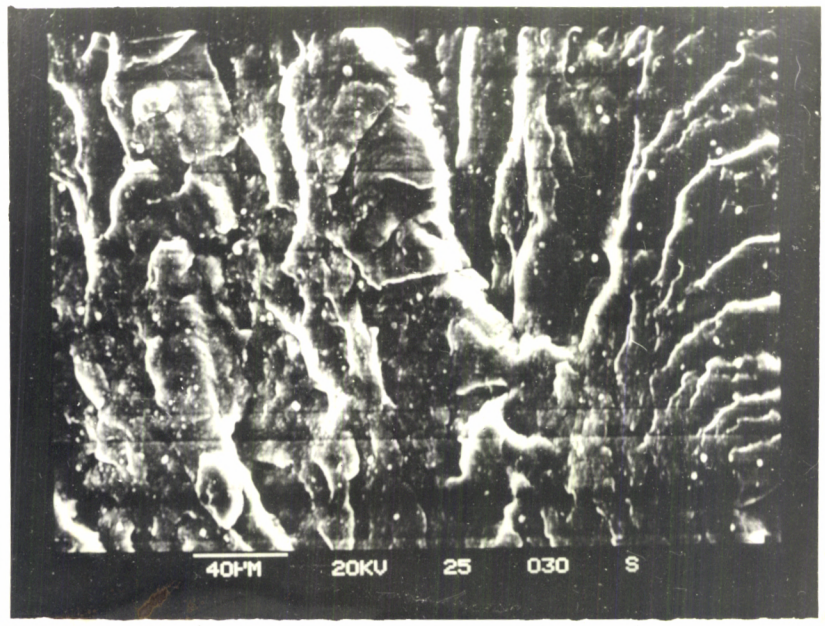


Fig.4.48 Force fed

SEM photograph of the tensile fracture surface of SBR vulcanizate.

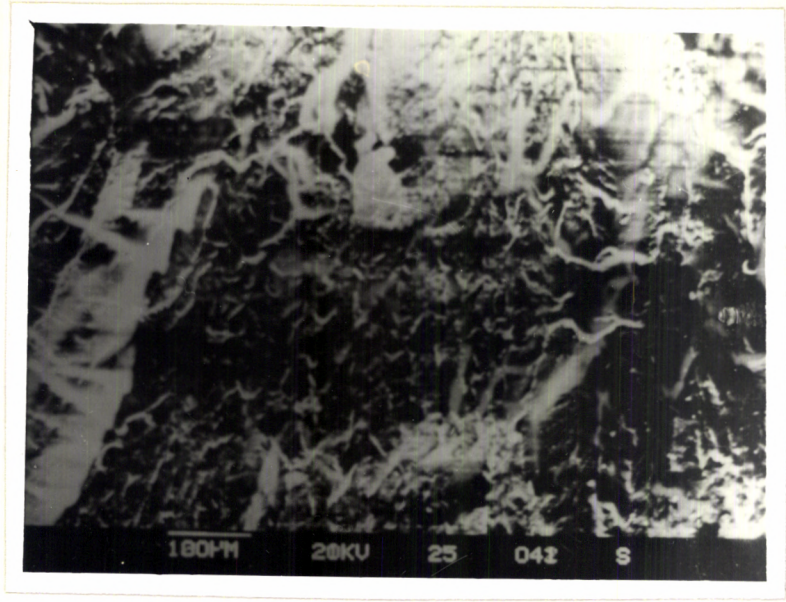


Fig.4.49 Starve fed

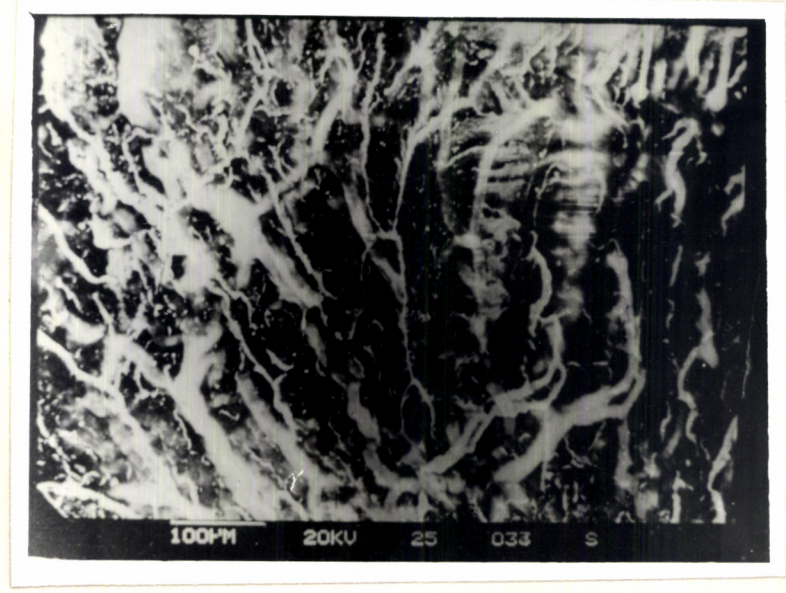


Fig.4.50 Flood fed

SEM photographs of the tensile fracture surfaces of IIR vulcanizates.

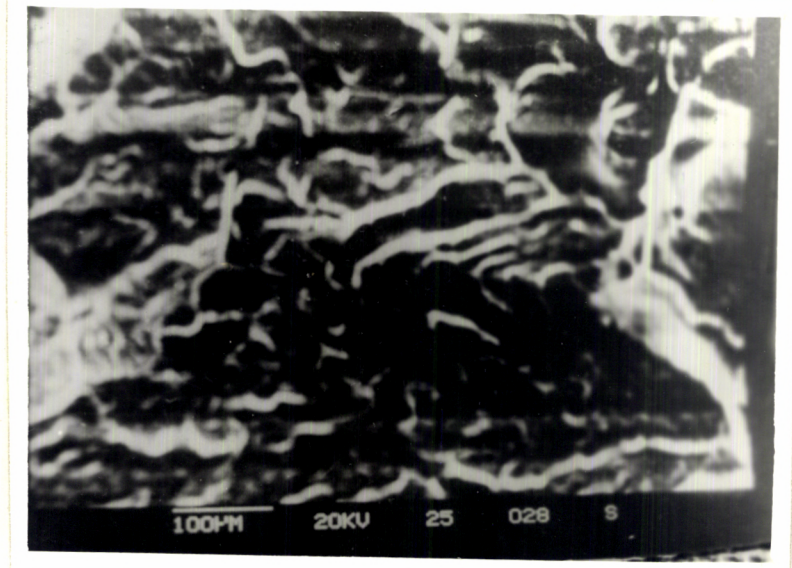


Fig.4.51 Force fed

SEM photograph of the tensile fracture surface of IIR vulcanizate.

less, but they are broader[33,34] compared to those in the flood fed and force fed samples. Generally, the starved sample shows a continuous orientation pattern arranged in a regular order, while such regularity is not observed in the case of flood fed and force fed samples.[35]

4.4 CONCLUSIONS

1. Feeding rate in the single screw extrusion of NR, SBR and IIR filled compounds affect the physical properties of their vulcanizates.

2. For a given screw there is an optimum feeding rate in the starved region which results in maximum physical properties.

3. Maximum physical properties are observed at a particular low level of starvation at each rpm and temperature.

4. The percentage of starvation at which maximum properties are observed decreases with either increase in rpm or increase in temperature.

5. The improvement in properties generally increases with increase in rpm and temperatures till thermal/shear degradation dominate the behaviour.

REFERENCES

1. R.Brozoskowski, J.L.White, F.C.Weissert, N.Nakajima, and K.Min, Rubber Chem. Technol., 59, 534 (1986).
2. G.Menges and J.Muller, Plastiverabeitor, 21, 305 (1970).
3. D.P.Isherwood, R.N.Pieris and D.Valamonte, Plast. Rubb. Processing Appl., 4, 257-260 (1984).
4. B.Ellis and G.N.Welding, "Techniques of Polymer Science", Soc. Chem. Ind., London, 46 (1964).
5. P.J.Flory and J.Rehnen, J. Chem. Phys., 11, 512 (1943).
6. B.Saville and A.A.Watson, Rubber Chem. Technol., 40, 100 (1967).
7. P.J.Joseph Francis, Rani Joseph and K.E.George, J. Elast. and Plast., 29, 149 (1997).
8. P.J.Francis, R.Joseph and K.E.George, Kautschuk Gummi Kunststoff, 10, 704–709 (1997).
9. T.L.Smith, Polym. Eng. Sci., 17, 129 (1977).
10. J.E.Mark, J.Chem. Edu., 58, 898 (1981).
11. W.W.Graessley, Adv. Polym. Sci., 16, 1 (1974).
12. G.Ronca and G.Allegra, J. Chem. Phys., 63, 4990 (1975).
13. J.M.Mckelvey, "Polymer Processing", Wiley, New York (1962).
14. A.P.Plochocki, S.K.Dey, and K.Wilczynski, Polym. Eng. Sci., 26, 1007 (1986).

15. R.B.Kirby, SPEJ., 18, 1273 (1962).

16. Krzysztof Wilczynski, "Evaluating Screw Performance in Extrusion", Nicholas P.Cheriminisof (Ed.), Marcel Dekker Inc., N.Y., Chap.3, (1983).

17. R.Brozoskowski, K.Kubota, K.Chung, J.L.White, F.C.Weissert, N.Nakajima and K.Min, Int. Polym. Process, 1, 130 (1987).

18. R.Brozoskowski and J.L.White, Int. Polym. Process, 2, 102 (1987).

19. A.V.Tobolsky, J.Appl. Polym. Sci., 27, 173 (1956).

20. E.J.Blackman and E.B.Mccall, Rubber Chem. Technol., 43, 651 (1970).

21. L.Bateman, C.G.Moore, M.Porter and B.Saville, "The Chemistry and Physics of Rubber-like Substances", L.Bateman (Ed.), Maclaren and Son Ltd., London, Chap.15, (1963).

22. R.Worthtsch, R.Schnabel and E.O.Reher, Plast. Kautsch, 38, 41-5 (1991).

23. F.Grajewski and J.Sunder, Kautsch. Gummi Kunstst. 42, 604-9 (1989).

24. P.J.Flory, "Principles of Polymer Chemistry", Cornell University Press, Ithaca, N.Y., 1953.

25. D.F.Twiss, J. Soc. Chem. Ind., 44, 1067 (1925).

26. G.Kraus, Adv. Polymer Sci., 8, 155 (1971).

27. Siegfried Wolff, Meng Jiauwang and Ewe-Hongton, Rubber Chem. Technol., 66, 163–175 (1993).

28. L.Engel, H.Klingele, G.W.Ehrenstein and H.Schaper, "An Atlas of Polymer Damage", Prentice Hall, New Jersey (1981).

29. R.J.White and E.L.Thomas, Rubber Chem. Technol., 57, 457 (1984).

30. E.Balcerzyk, J.Hochstim and S.Wlodarezyk, Int. Polym. Sci. Technol., 12, 121 (1985).

31. R.Joseph, K.E.George and D.Joseph Francis, J. Appl. Polym. Sci., 35, 1005 (1988).

32. R.Joseph, K.E.George and D.Joseph Francis, Angew. Makromol. Chem., 152, 107–119 (1987).

33. N.M.Mathew, A.K.Bhowmick, B.K.Dhindaw and S.K.De, J. Mater. Sci., 17, 2594–98 (1982).

34. H.W.Greensmith, J. Appl. Polymer Sci., 3, 175–183 (1960).

35. P.J.Joseph Francis, Rani Joseph and K.E.George, Iranian Polymer Journal 6(1), 19–26 (1997).

CHAPTER 5

EFFECT OF FEEDING RATE ON THE MECHANICAL PROPERTIES OF LDPE AND PS

Part of the work presented in this chapter has been accepted for publication in International Journal of Polymeric Materials.

EFFECT OF FEEDING RATE ON THE MECHANICAL PROPERTIES OF LDPE & PS

5.1 INTRODUCTION

Single screw extrusion is among the fastest developing methods for processing polymers. In the process of extrusion, the molten polymer is subjected to relatively high shear rates and temperatures.[1] During deformation, viscous heat is dissipated due to the friction between the highly viscous polymer melt and the various parts of the processing equipment that it comes in contact with. The viscous heat dissipated leads to a temperature rise, resulting in an offset of the setting the extruder temperature profile with respect to throughput rate.[2] All high output rate operations such as flood fed and force fed extrusions, since large viscous heat is generated, result in non-uniform heat generation. The problem is accentuated due to the very low thermal conductivity of the polymer melts. This may lead to polymer degradation[3,4], which in turn reduce the polymer properties.

It was observed that the feeding rate has a profound effect on the mechanical properties of the vulcanizates of extruded rubber compounds and that maximum properties are observed at a particular feeding rate in

the starve fed region. This was found to be mainly due to the uniformity in temperature and shear at that low level of starve feeding.[5] Feeding rate may influence the mechanical properties of thermoplastics also and this study has been undertaken for investigating this possibility.

Two widely used plastics one which is semicrystalline, low density polyethylene (LDPE) and another one which is amorphous, polystyrene (PS) were selected for the study.

5.2 EXPERIMENTAL

Extrusion studies were done on a laboratory general purpose plastic extruder attached to a Brabender plasticorder model PL 2000 with an L/D ratio of 25, a compression ratio of 2 and provided with a hopper for feeding. Two widely used standard thermoplastics viz., LDPE and PS were selected for the study.

A vibratory feeder in conjunction with a voltage stabilizer was used for metering the solid pellets of LDPE and PS, so that the polymer from the hopper fell directly into the throat of the extruder feed section port. The feeding rates were adjusted by changing the dimension of the feed gap at the bottom of the hopper and measured by the rate of output of the extrudate.[6]

The compounds were extruded at varying feeding rates mainly in the starve fed region and then in the flood fed and force fed regions at 20, 40, 60 and 80 rpms and at different temperatures. The force feeding was done by applying controlled pressures on the material in the hopper. The dumb bell specimens were cut out of the extruded sheet for tensile testing. The tensile properties of the extrudates were measured using a Zwick universal testing machine model 1445, both in extrusion and in its transverse directions at an extension rate 50 mm/min. as per ASTM standards. From the feeding rates at the flood fed level and starve fed levels, the percentage of starvation was calculated.[7] Temperature and flow rate fluctuations during extrusion were noted.

The thermogravimetric analysis (TGA) of the starve fed, flood fed and force fed extrudate samples of LDPE and PS were carried out in a Du–Pont–2000 thermal analyzer in nitrogen atmosphere at a heating rate of 10°C/min. The density of the starve fed, flood fed and force fed sheets was measured according to relevant ASTM standard. The differential scanning calorimetry (DSC) curves of the above samples of LDPE and PS were carried out on a Mettler TA–3000 model at a heating/cooling rate of 10°C/min. under nitrogen atmosphere as per ASTM standards. The viscosity of the solutions of the starve fed, flood fed and force fed samples of LDPE and PS were measured using a Brookfield viscometer according to ASTM standards.

The morphology of LDPE and PS samples were investigated by using an optical microscope (Versanet–2 Union 7596) at a magnification of 330. The tensile fracture surfaces of a few typical samples of LDPE and PS were examined using a scanning electron microscope of model Stereoscan 250 MK3 Cambridge instrument to study the mode of failure.

5.3 RESULTS AND DISCUSSION

5.3.1 Torque

Figure 5.1 shows the variation of torque with feeding rate for LDPE at 180°C at different rpms of 20, 40, 60 and 80. It is found that the extrusion torque gets progressively reduced with increase in the starvation level. The percentage reduction of torque between the flood feeding point and the lowest feeding point is up to 43% in the case of LDPE at the various rotational speeds of the screw.

Figure 5.1 also shows the variation of torque with feeding rate for PS at 220°C at different rpms of 20, 40, 60 and 80. As in the case of LDPE, the reduction of torque between the flood feeding point and the lowest feeding point is up to 34% at different screw speeds.

Figure 5.2 shows the variation of torque with feeding rate for LDPE and PS at different temperatures and at a fixed rpm of 40. In the case of LDPE when the temperature increases from 160°C to 220°C, the

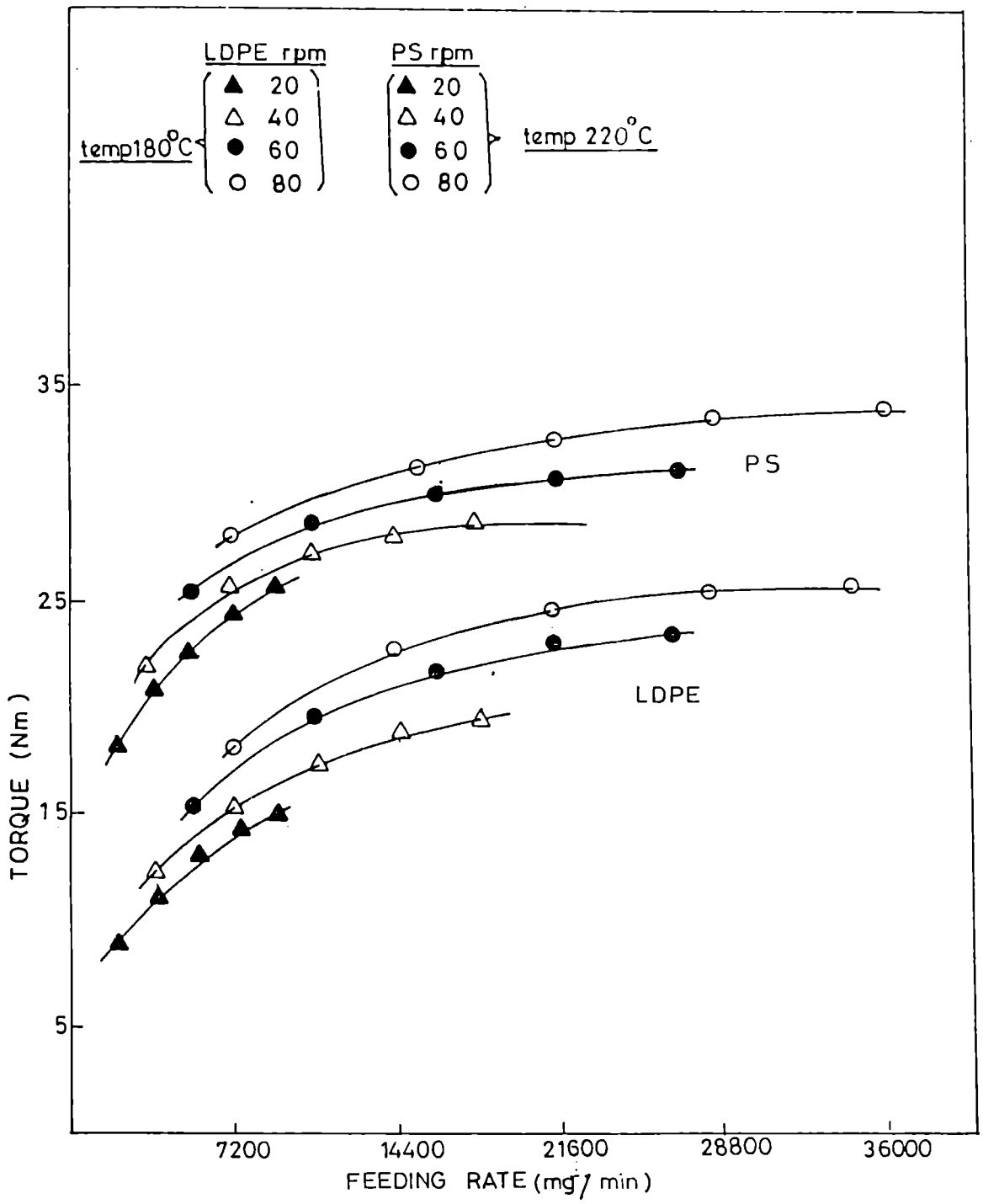


Fig.5.1 Variation of torque in the extrusion of LDPE and PS with feeding rate at different rpm.

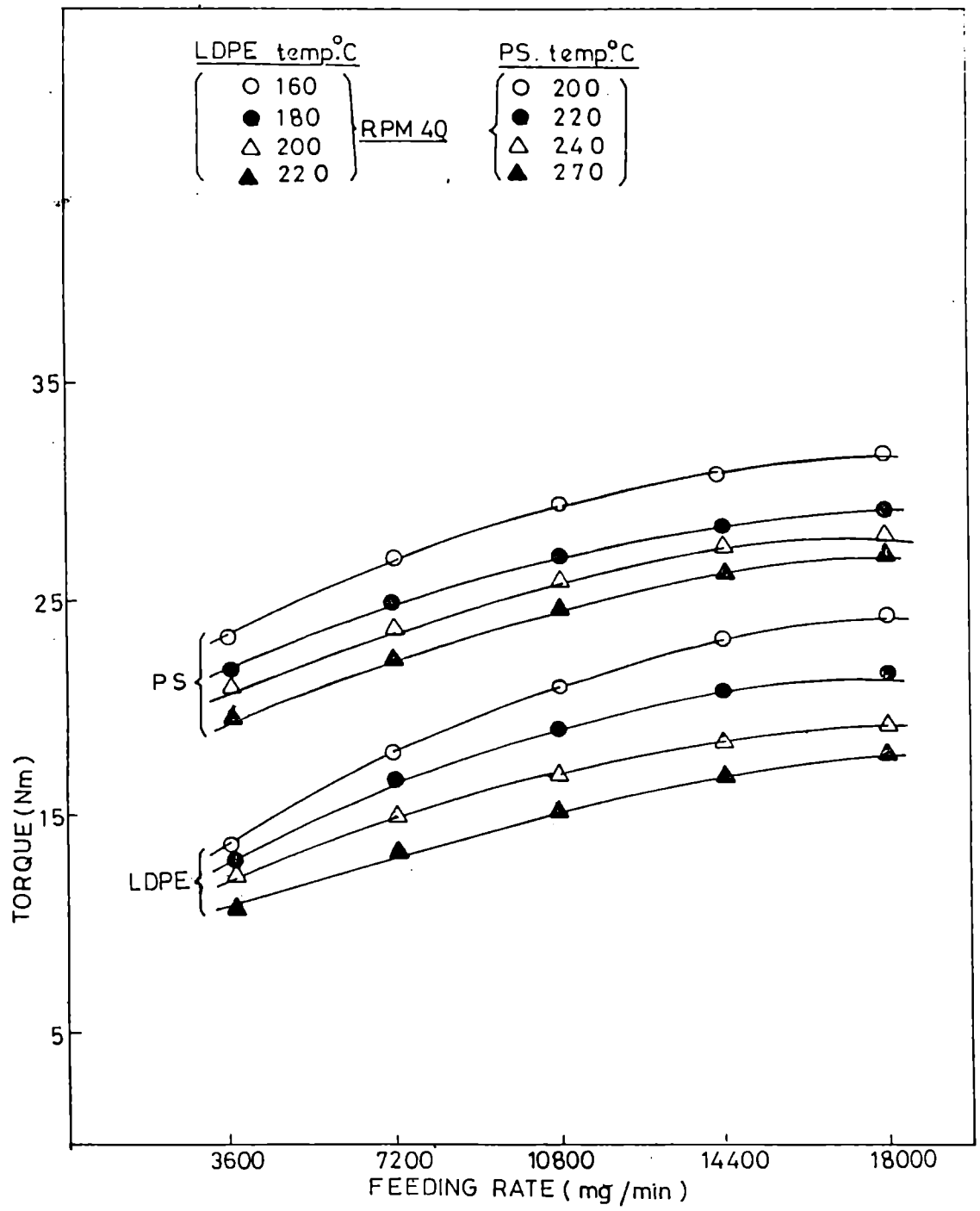


Fig.5.2: Variation of torque in the extrusion of LDPE and PS with feeding rate at different temperatures.

reduction of torque between the flood feeding rate and the lowest feeding rate is up to 42%. But in the case of PS when the temperature ranges from 200°C to 270°C, the reduction of torque between the flood feeding rate and the lowest feeding rate is only up to 31%.

The figures show that the torque required for extrusion can be substantially brought down by operating in the starved region or employing higher temperatures. Table 5.1 shows the variation of reduction of torque with percentage of starvation.

5.3.2 Tensile properties

Figure 5.3 shows the variation of tensile strength with feeding rate at different rpms for LDPE at a temperature of 180°C and PS at a temperature of 220°C. The point of maximum feeding rate in each curve of the figure represents the force feeding point. The feeding rate just below the force feeding point represents the flood feeding point. Other points are in the starve fed region. It is found that irrespective of rpm the tensile strength initially increases with feeding rate, reaches a maximum and thereafter decreases. This shows that for a given shear rate and temperature, there is a particular feeding rate in the starved region just below the flood feeding point which results in maximum tensile strength. This obviously results from the improved uniformity in temperature and better homogeneity[8] of the compounds than that in flood feeding (normal feeding) and in force feeding (power feeding). Further,

Table 5.1 Variation of the percentage reduction in torque with percentage of starvation

% Starvation	% Reduction in torque of LDPE			% Reduction in torque of PS		
	At 20 rpm and at 180°C	At 60 rpm and at 180°C	At 40 rpm and at 220°C	At 20 rpm and at 220°C	At 40 rpm and at 220°C	At 40 rpm and at 270°C
75	43.2	37.4	42.0	34.1	29.3	31.1
50	32.4	30.3	35.2	27.6	24.5	25.6
25	23.1	23.7	26.8	22.4	19.0	20.5
10	15.5	14.2	18.0	16.7	12.5	15.0
0 (Flood feeding)	--	--	--	--	--	--

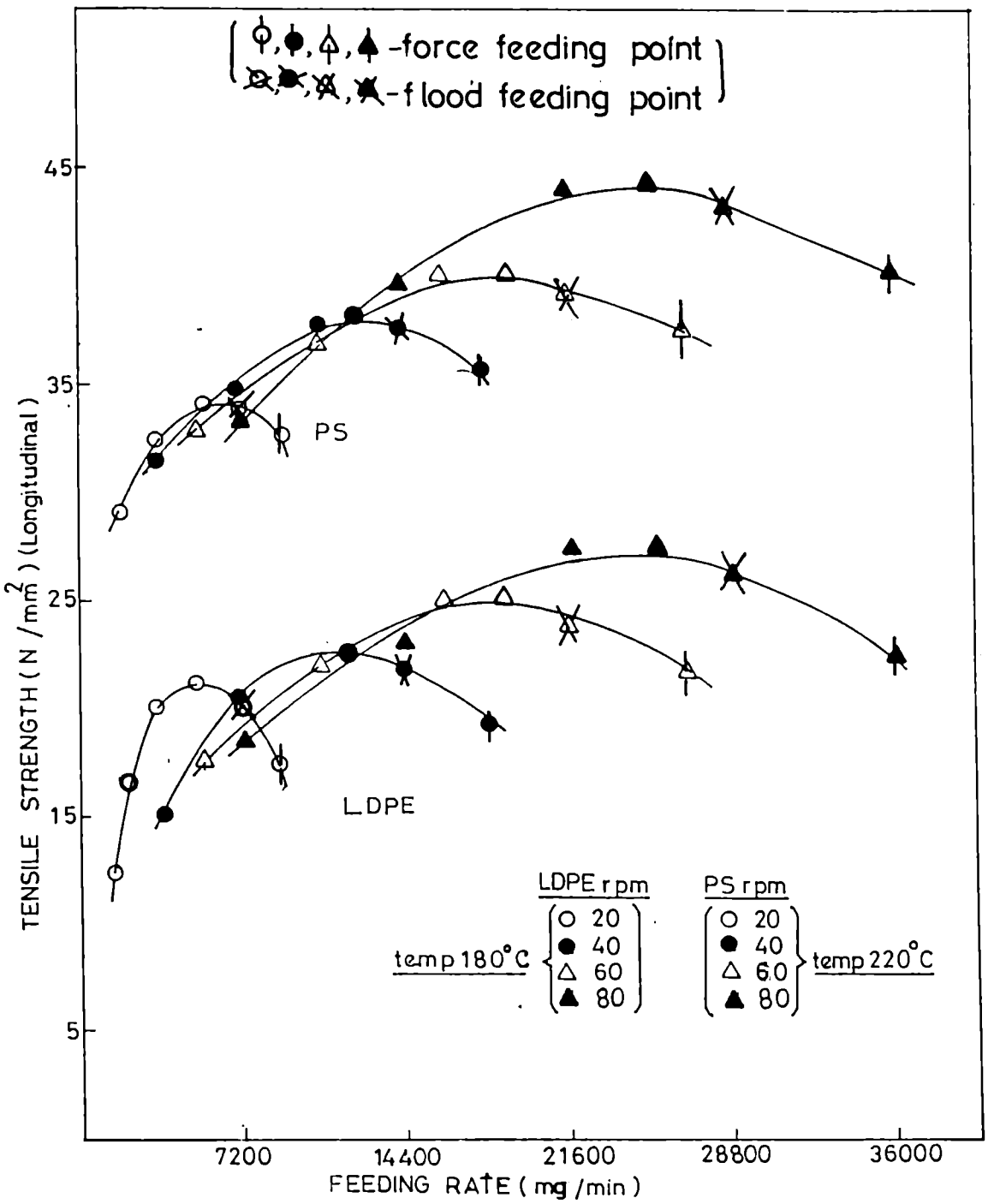


Fig.5.3: Variation of tensile strength of LDPE and PS with feeding rate at different rpm in the extrusion direction.

lower shear breakdown and preferential orientation[9] of the molecules may be other reasons for the higher tensile strength at this feeding rate. The preferential orientation effect is clearly seen from the large differences between the tensile strength measured in the extrusion and transverse directions in this case (Figs. 5.3 and 5.4).

Figures 5.5 and 5.6 show the variation in elongation at break of LDPE and PS with feeding rate in the extrusion and transverse directions at different rpms. As in the case of tensile strength unimodel curves are obtained for each rpm. This further shows the efficiency of starved extrusion in getting maximum physical properties.

Isherwood et al.[7,10] suggest that looser packing of the material in the channels in the starve feeding region results in greater bed mobility. Hence, high bed temperatures are not built up at the bed-to-barrel interface as in the case when the bed is densely compacted. In addition, since the bed is more flexible it does not snap under the influences of forces on it giving a smoother profile.

Figures 5.7 and 5.8 show the variation in tensile strength of LDPE and PS with feeding rate in the extrusion and transverse directions at different temperatures, at fixed rpm. The tensile strength improves with temperature when the temperature is raised from 160°C to 200°C in the case of LDPE and from 200°C to 240°C

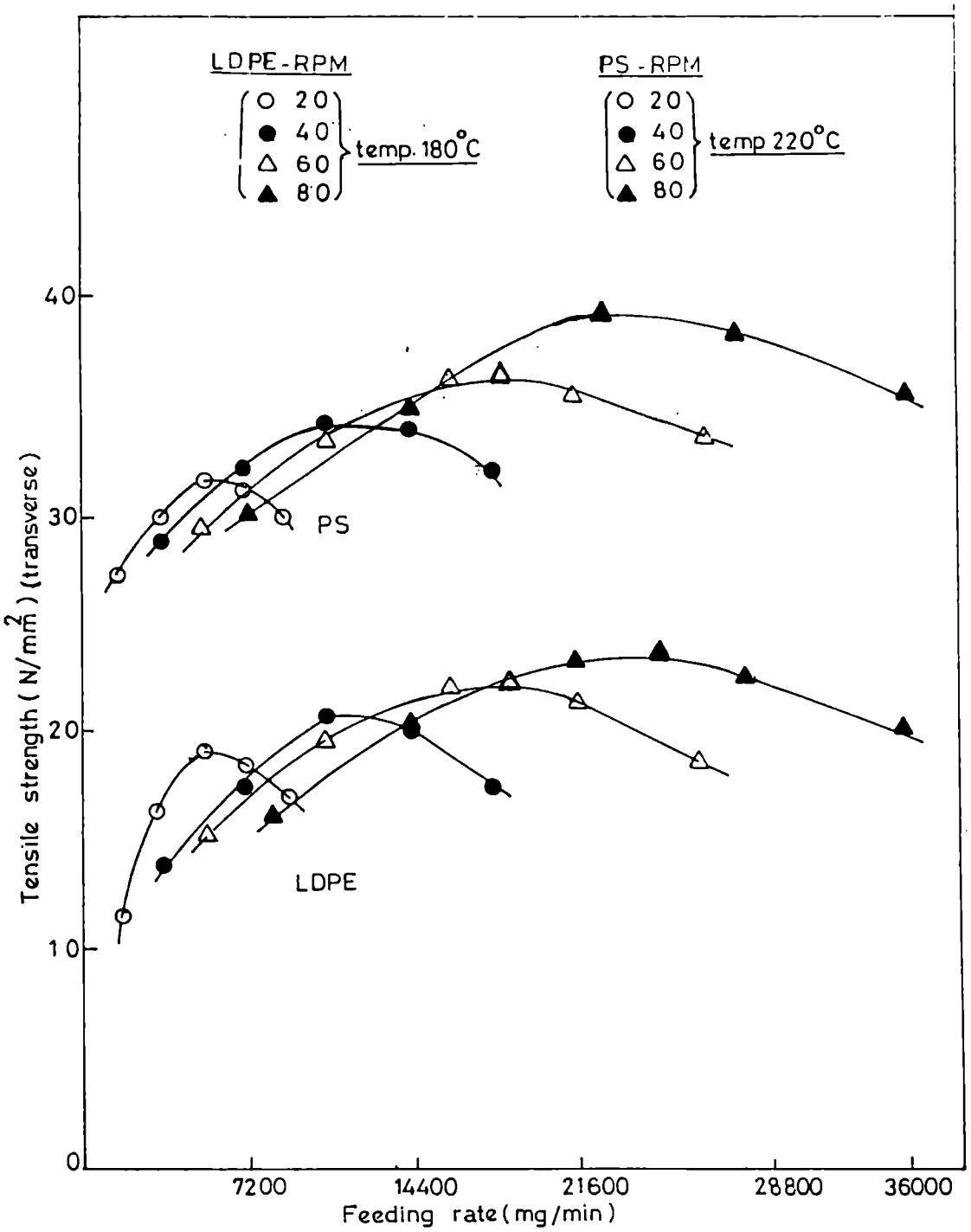


Fig.5.4: Variation of tensile strength of LDPE and PS with feeding rate at different rpm in the transverse direction.

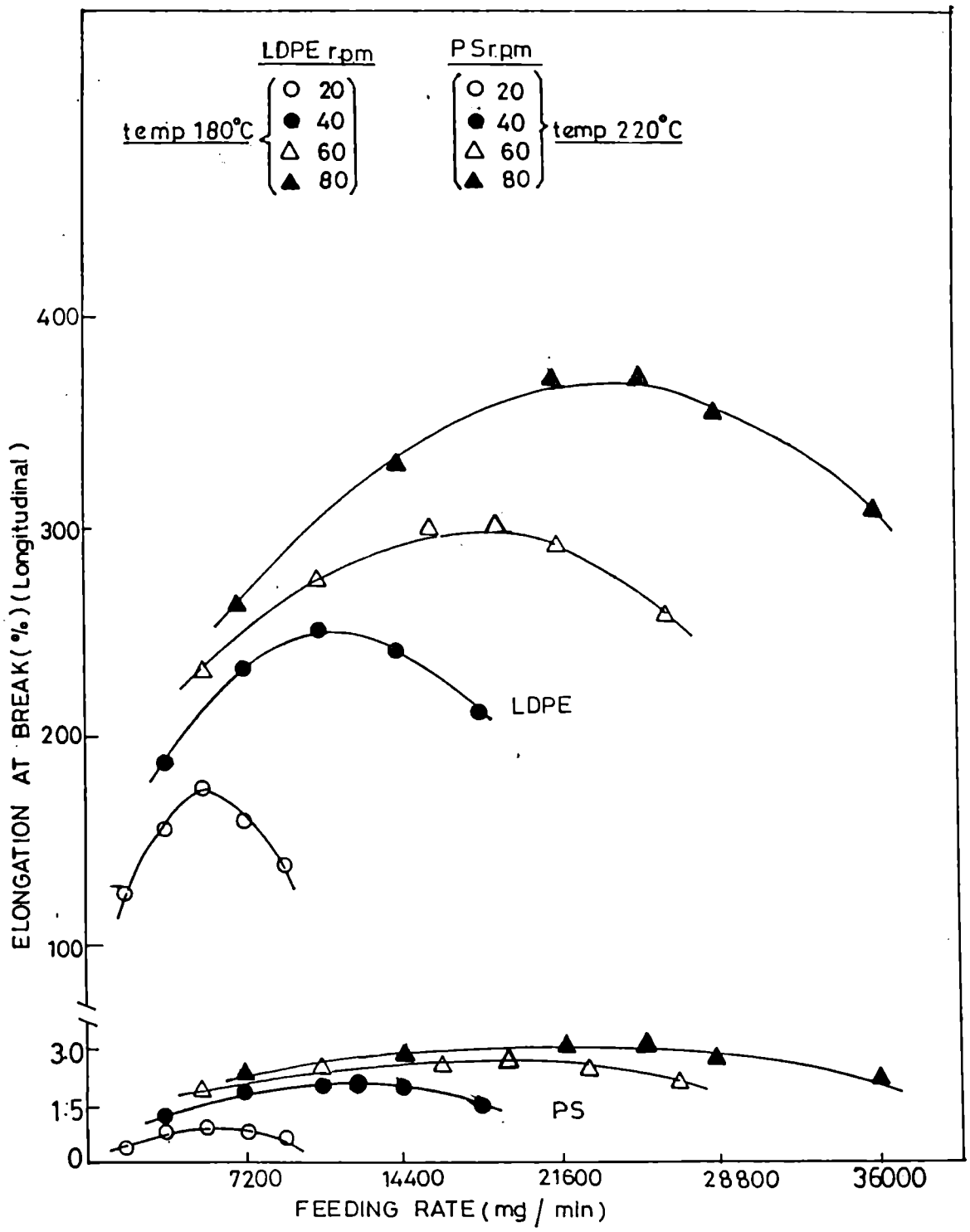


Fig.5.5: Variation of elongation at break of LDPE and PS with feeding rate at different rpm in the extrusion direction.

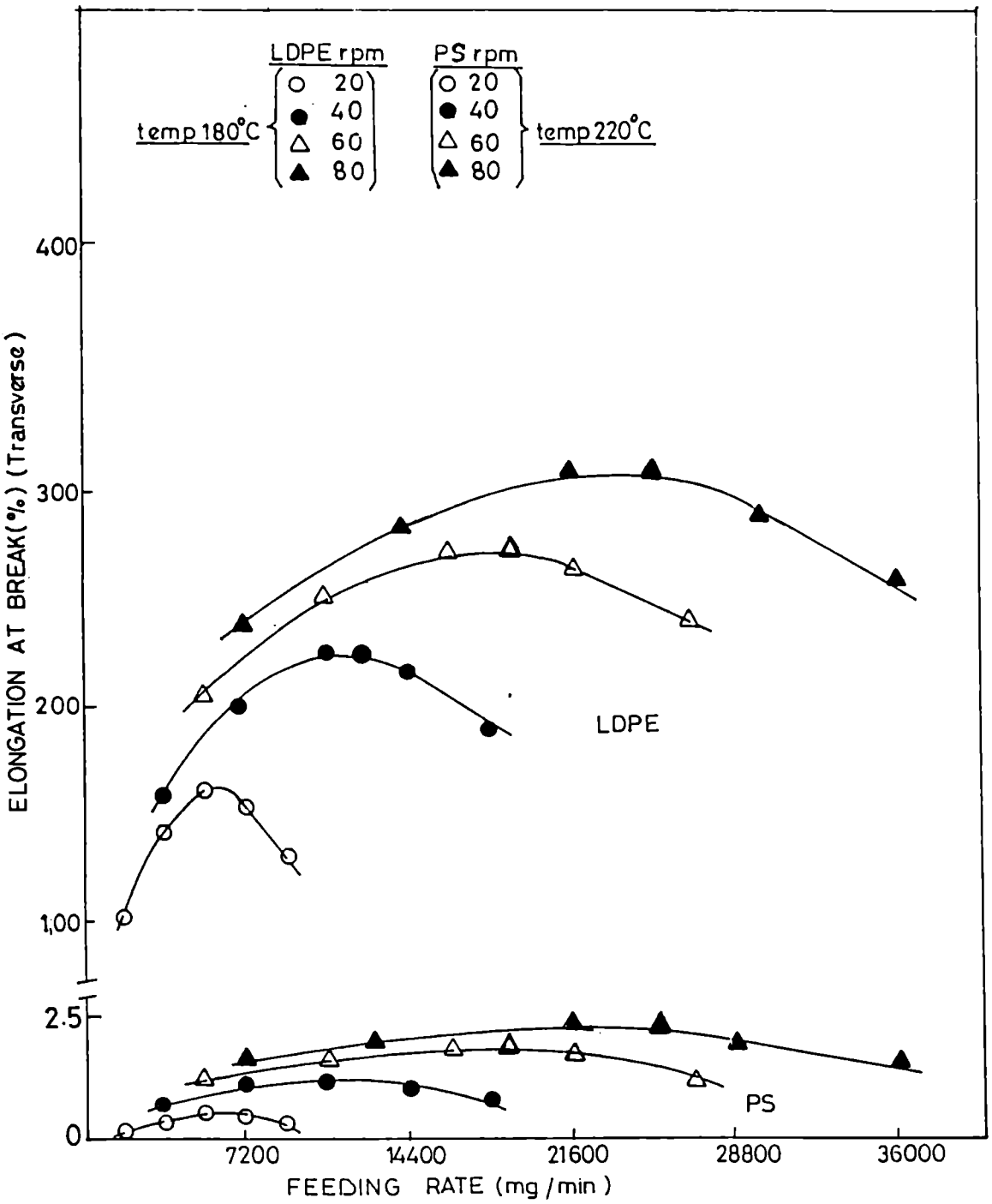


Fig.5.6: Variation of elongation at break of LDPE and PS with feeding rate at different rpm in the transverse direction.

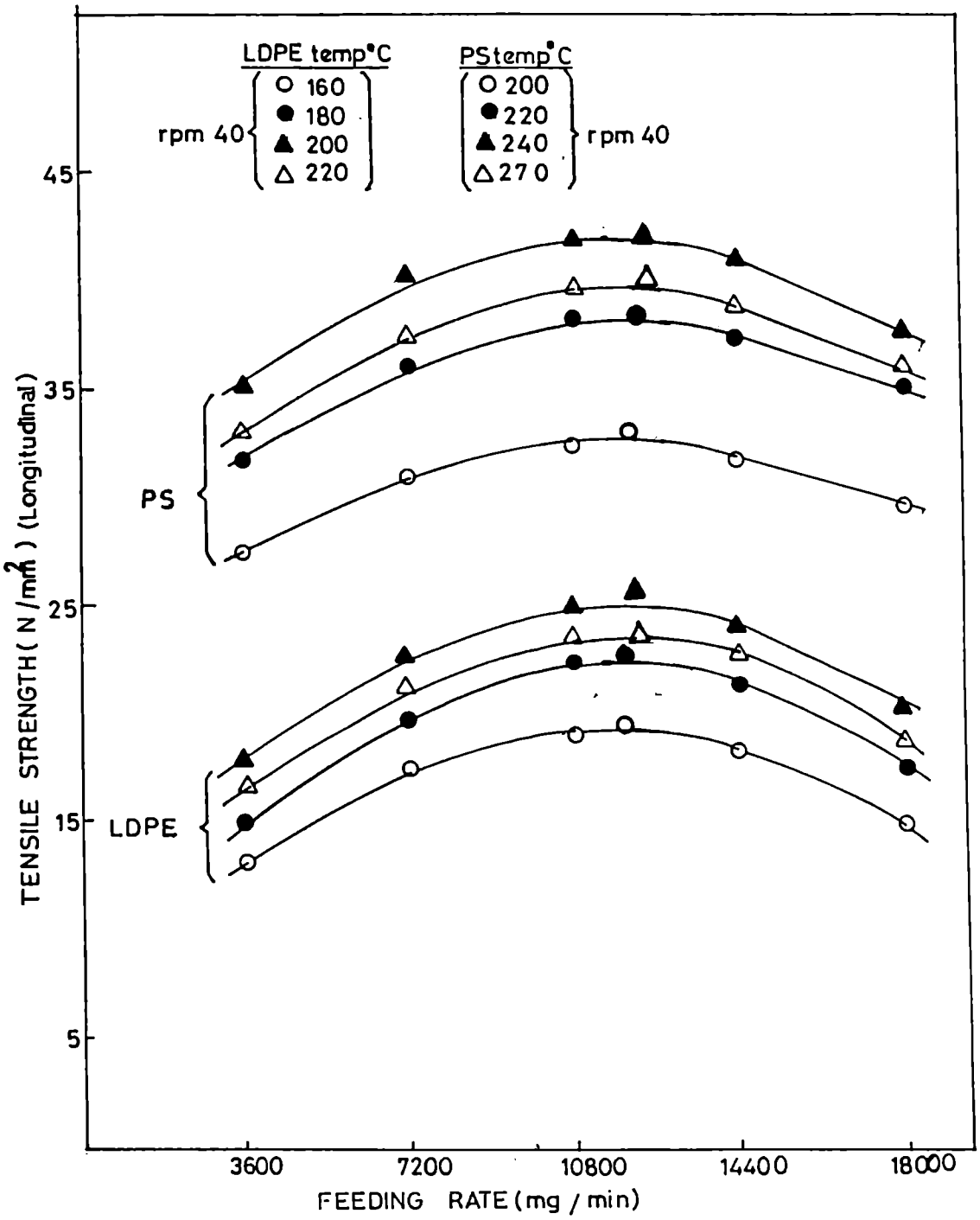


Fig.5.7: Variation of tensile strength of LDPE and PS with feeding rate at different temperatures in the extrusion direction.

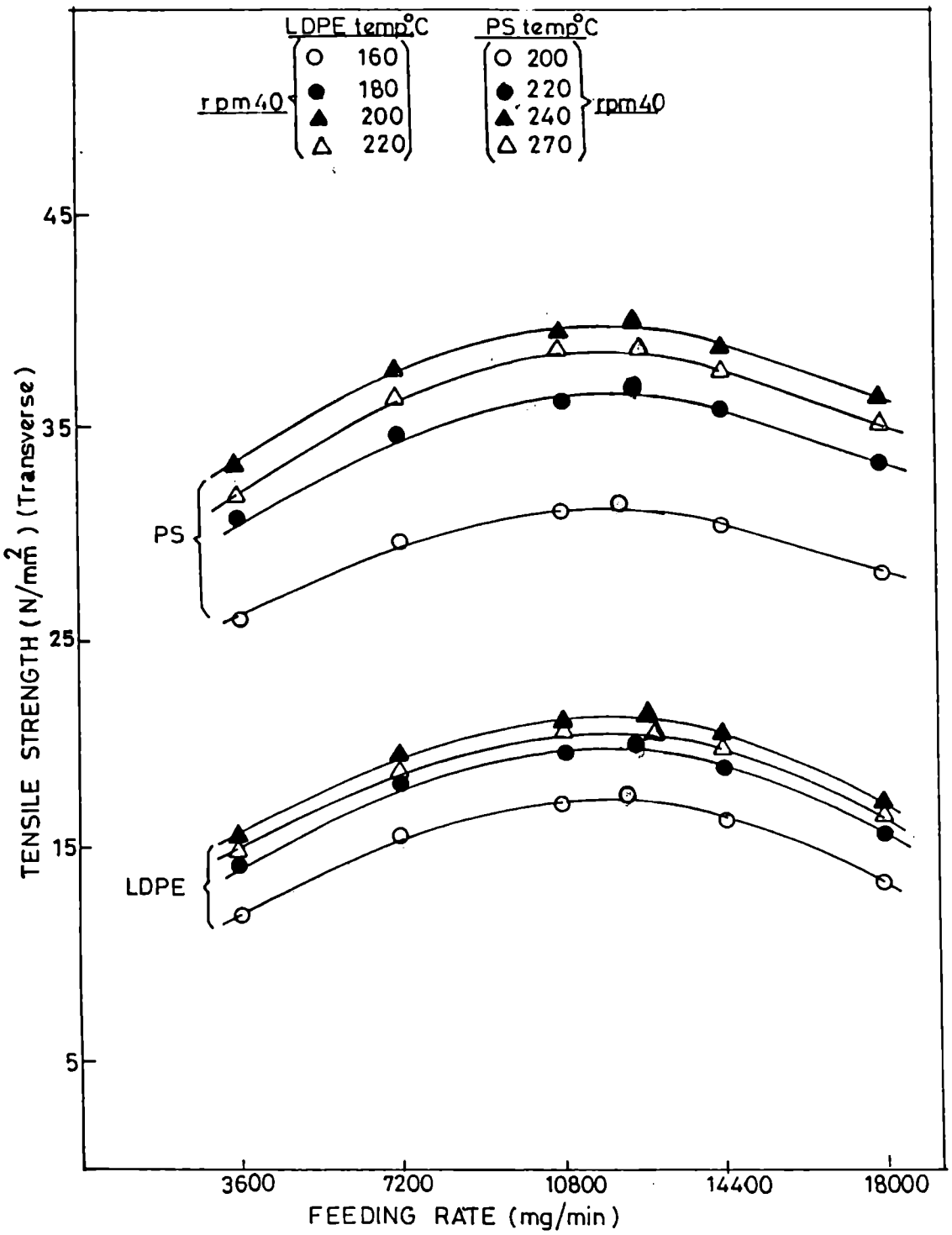


Fig.5.8: Variation of tensile strength of LDPE and PS with feeding rate at different temperatures in the transverse direction.

in the case of PS in the starved region, showing that deterioration due to thermal degradation is not serious in this range. This result is expected since PS is more thermally stable than LDPE.[11] But the strength at 220°C is less than at 200°C in the case of LDPE and the strength at 270°C is less than at 240°C in the case of PS showing the onset of degradation. At every temperature, the strength increases with feeding rate, reaches a maximum and decreases thereafter. As before, the maximum occurs just below the flood feeding point in the range 160–200°C and further down at 220°C in the case of LDPE. In the case of PS, maximum tensile strength occurs just below the flood feeding point in the temperature range 200–240°C and further down at 270°C. Figures 5.9 and 5.10 show the variation in elongation at break with feeding rate at different temperatures at a fixed rpm in the extrusion and transverse directions of LDPE and PS. The behavior is more or less similar to that of the variations of the tensile strength.

In the above cases (shown in the Figs. 5.3–5.10) it is found that at the flood feeding point, the tensile properties begin to decrease. At the force fed point the tensile properties decrease further. This may be due to the non-uniform shear and temperature distributions that occur in the flood fed and force fed levels. The non-uniform shear and temperature distribution affects the uniform melting. Generally the melting efficiency of screws is decreased by phenomena associated with the existence of relatively thick melt layers that are in contact with the solid bed namely

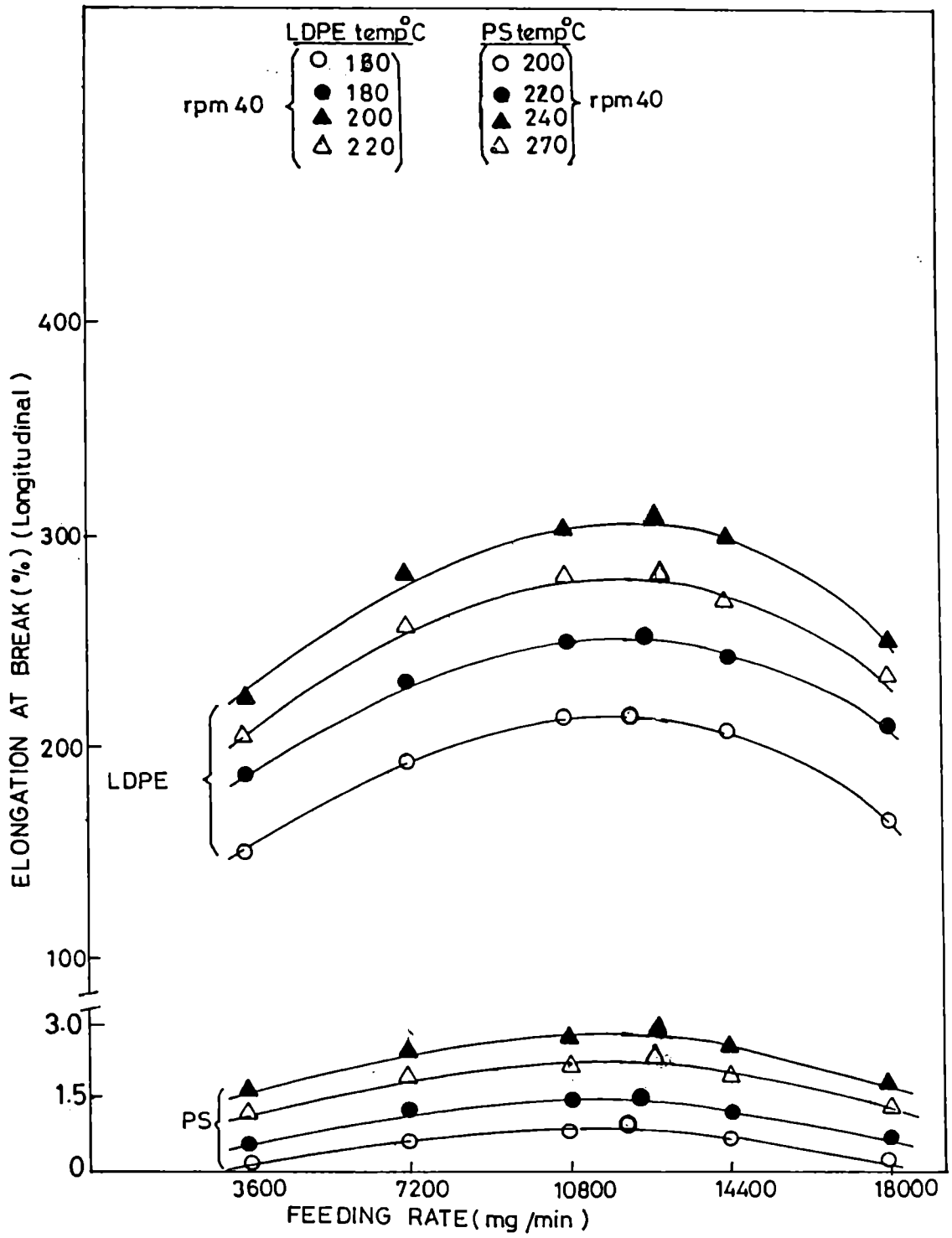


Fig.5.9: Variation of elongation at break of LDPE and PS with feeding rate at different temperatures in the extrusion direction.

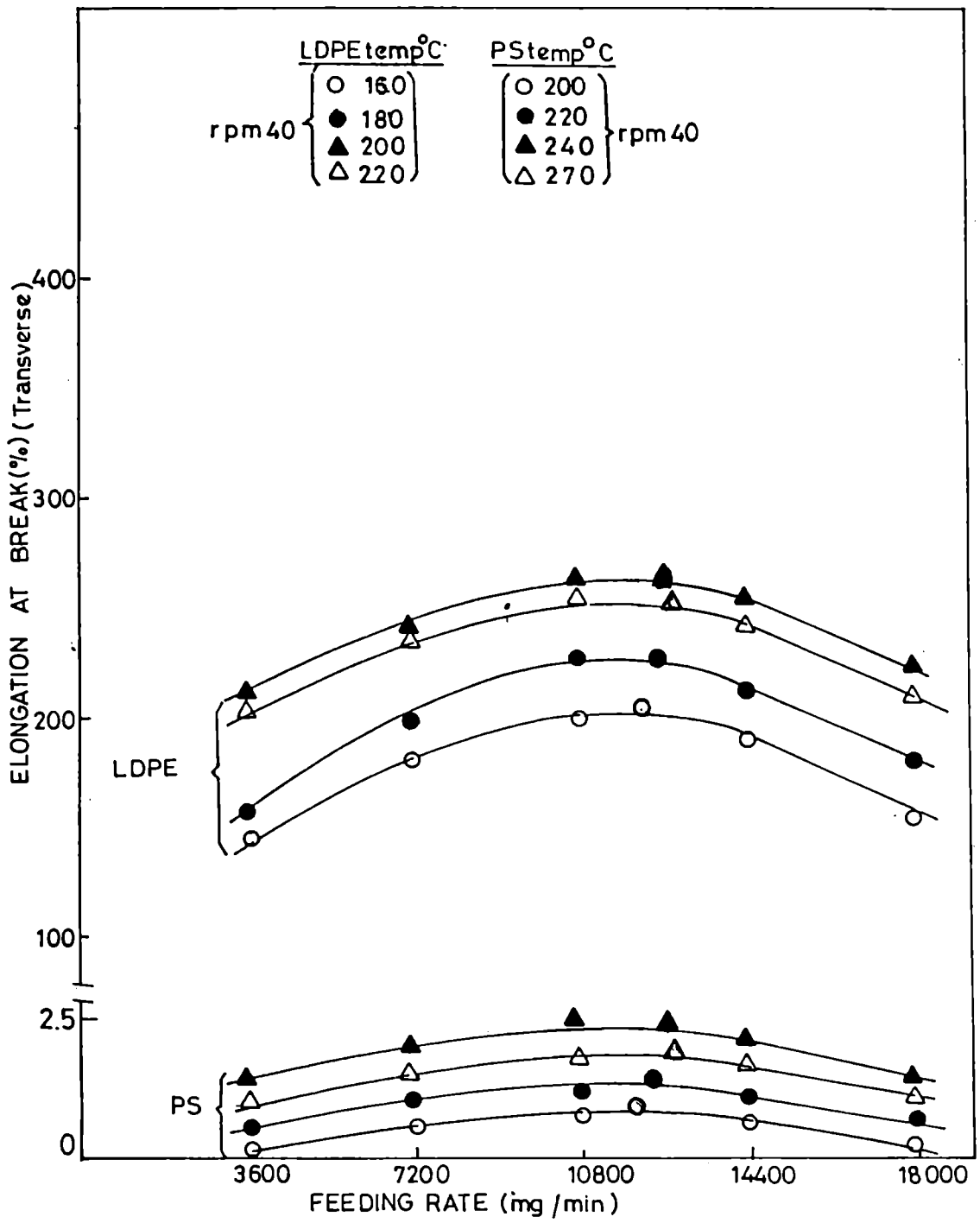


Fig.5.10: Variation of elongation at break of LDPE and PS with feeding rate at different temperatures in the transverse direction.

'the meltpool' and the melt film at the screw surfaces.[12] Their presence introduces an appreciable heat transfer resistance and even more importantly, may cause the solid bed to break up. Non-uniform melting may affect uniform mixing[10,13,14] which may also lead to mechanical degradation mainly in the flood fed and force fed regions.

For most screws the output rate increases linearly with screw speed, while melting capacity increases non–linearly.[15-17] It is possible to change the position of the level of feeding by changing the screw speeds. But at low screw speeds, melting rate rises sharply, generally exceeding the pumping rate, but at greater screw speeds this exceeds melting capacity, the screw pumps more than it can melt delivering a non-homogeneous extrudate, but of course contribute to degradation of the material.[18,19] But there may be a region at which the pumping rate and melting capacity may get even resulting in a homogeneous extrudate. That homogenization point is at a feeding rate which results in maximum physical properties.

5.3.3 Percentage of starvation and tensile properties

Figure 5.11 shows the variation of tensile strength and elongation at break of LDPE with percentage of starvation at rpms 20, 40, 60 and 80 at a fixed temperature of 180°C. At 20 rpm the maximum tensile properties are obtained at a percentage starvation of 17%. At 40, 60 and 80 rpms the maximum tensile properties are obtained at 15%, 14% and

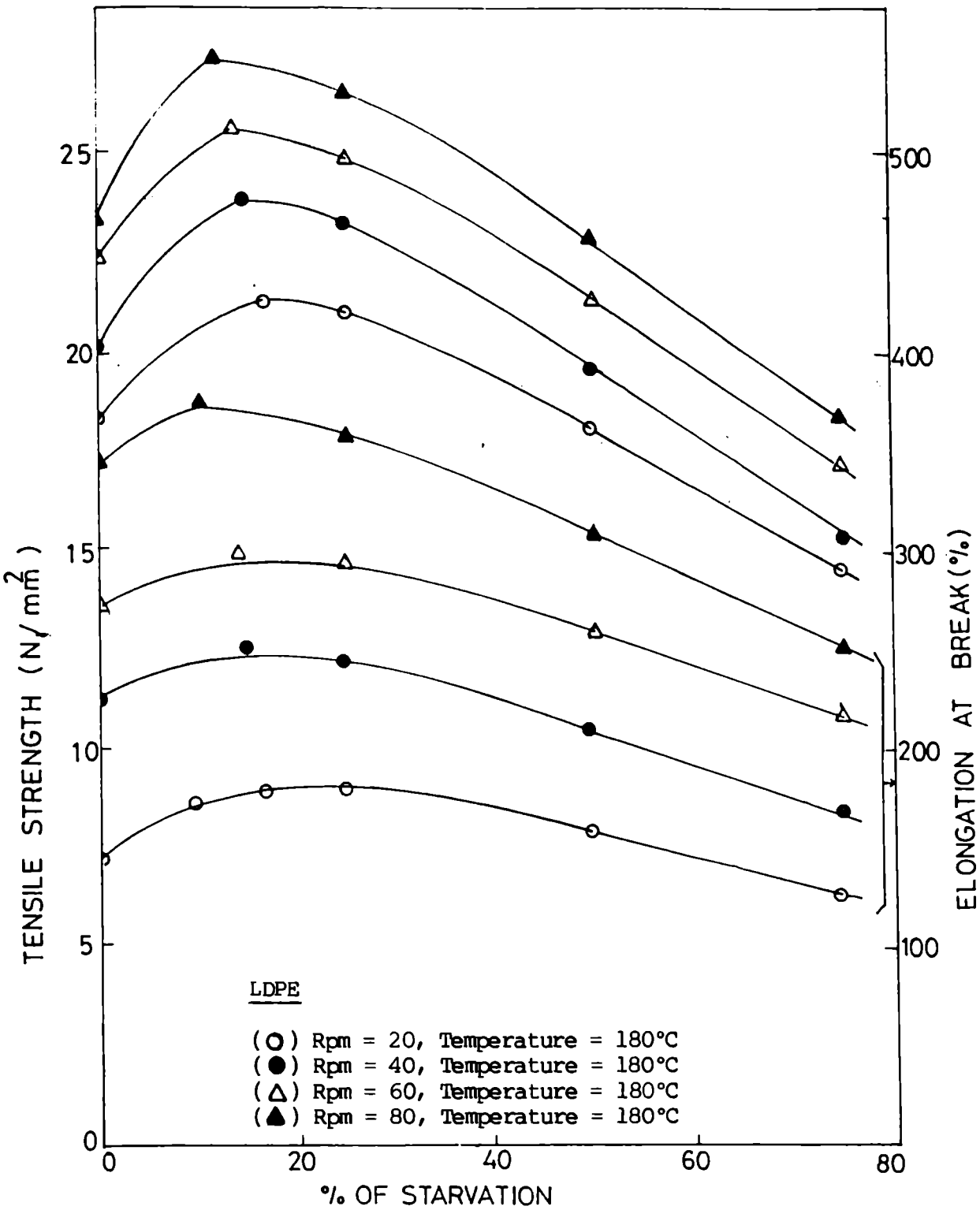


Fig.5.11: Variation of tensile strength and elongation at break of LDPE with percentage starvation at different rpm.

12% of starvation respectively. This shows that the percentage of starvation level at which maximum tensile properties obtained is gradually decreased with increase in rpm.

Figure 5.12 shows the effect of percentage starvation on the tensile strength and elongation at break of PS at different rpms at a fixed temperature of 220°C. As in the case of LDPE, the tensile properties gradually increase with increase in the feeding rate reach a maximum value and then decreases. It is found that at 20, 40, 60 and 80 rpms, the maximum tensile properties are observed at 12%, 11%, 10% and 9% of starvation respectively. This further shows that the percentage of starvation at which maximum tensile properties are obtained decreases with increase in rpm.

The variation of tensile properties of LDPE with percentage of starvation at different temperatures of 160°C, 180°C and 200°C at a fixed rpm of 40 is shown in the Fig.5.13. Here also it is found that the tensile properties increase with feeding rate and reach a maximum value and then decreases with further increase in feeding rate. It is found that at starvation levels of 16%, 15% and 12% the maximum tensile properties are obtained at temperatures, 160°C, 180°C and 200°C respectively. This shows that the percentage of starvation at which maximum properties are obtained decreases with increase in temperature.

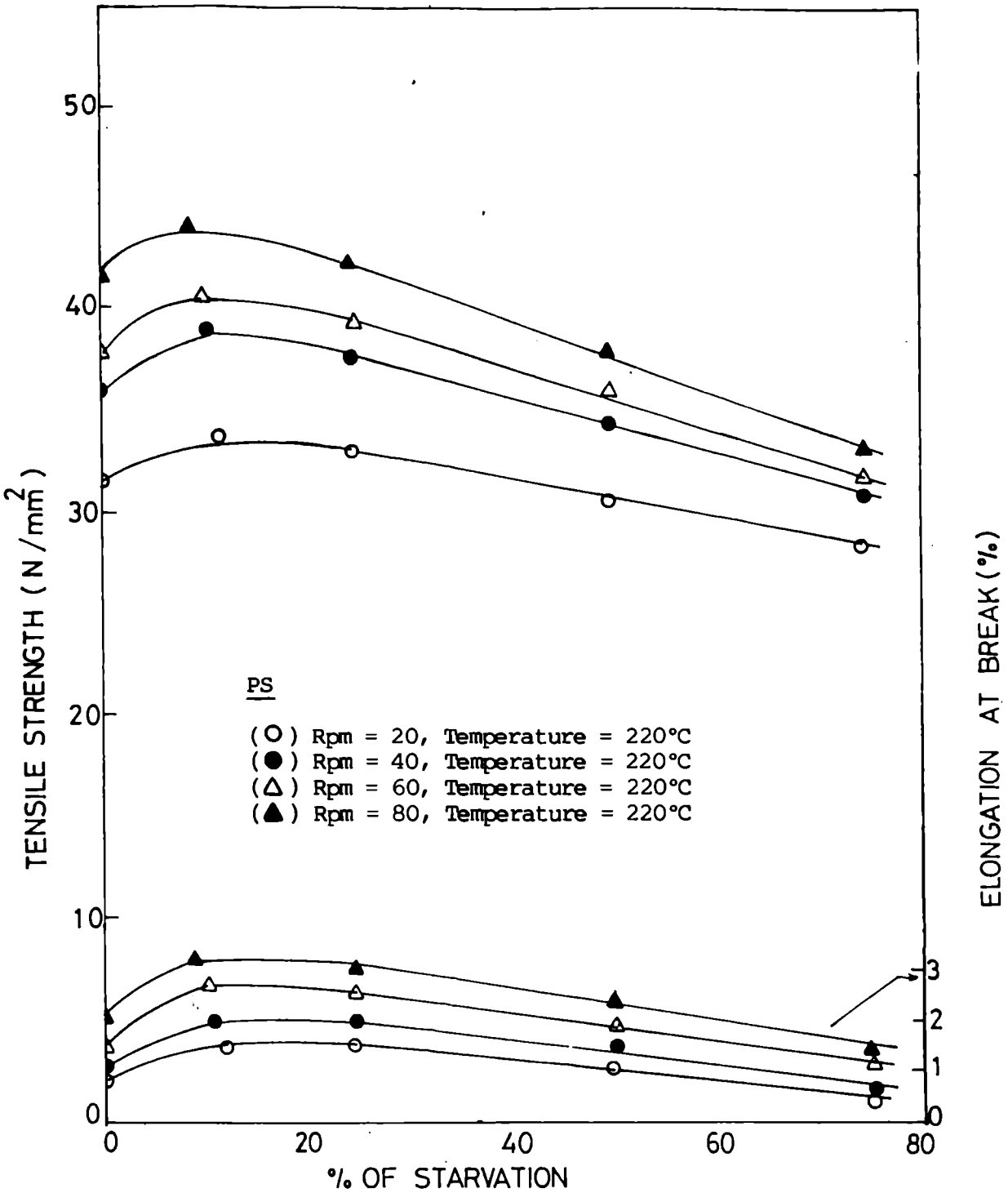


Fig.5.12: Variation of tensile strength and elongation at break of PS with percentage of starvation at different rpm.

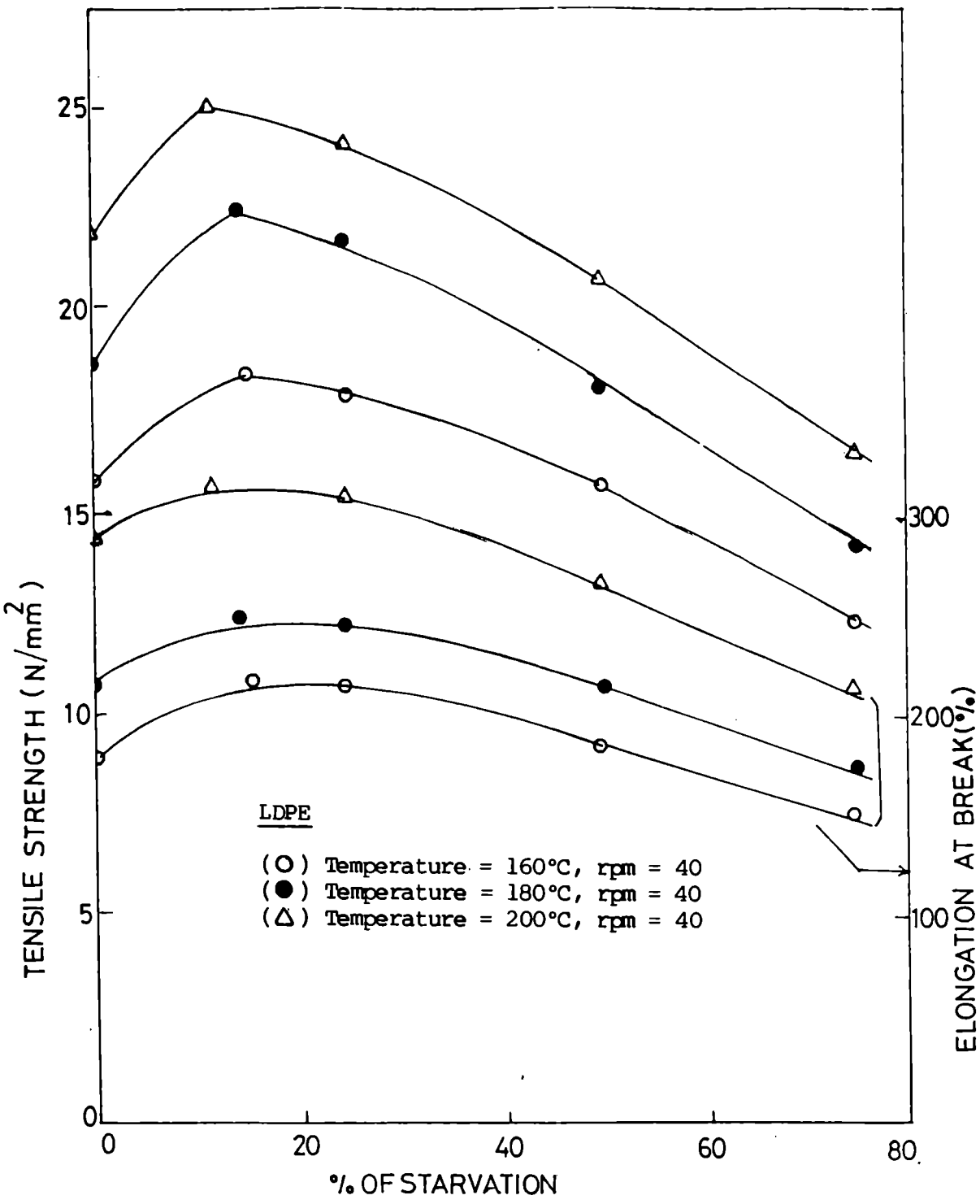


Fig.5.13: Variation of tensile strength and elongation at break of LDPE with percentage of starvation at different temperatures.

Figure 5.14 shows the variation of tensile properties of PS with percentage of starvation at different temperatures 200°C, 220°C and 240°C at a fixed rpm of 40. As in the case of LDPE unimodel curves are obtained and it is observed that the maximum tensile properties are obtained at starvation levels of 13%, 11% and 9.5% respectively at temperatures of 200°C, 220°C and 240°C. This further shows that the percentage of starvation at which maximum tensile properties are obtained decreases with increase in temperature.

5.3.4 Effect of extrusion variables

As pointed out earlier the quality of the extrudates depends substantially on the fluctuation of main variables of the extrusion process (variability of these parameters in time at a definite space point). If the fluctuations of temperature, flow rate and pressure are greater than permissible the properties of the extrudates will not be uniform and hence the properties may be inferior.[20] Fluctuations of temperature, pressure and flow rate are not phenomena independent of one another. For example, pressure fluctuations lead to flow rate fluctuations and can themselves be produced by temperature fluctuations, as a result of viscosity variations.[21] In the light of the results of investigations, the most independent phenomenon is temperature fluctuation and it is mainly for this reason that this property has been taken as the most important criterion of screw performance evaluation and hence quality of

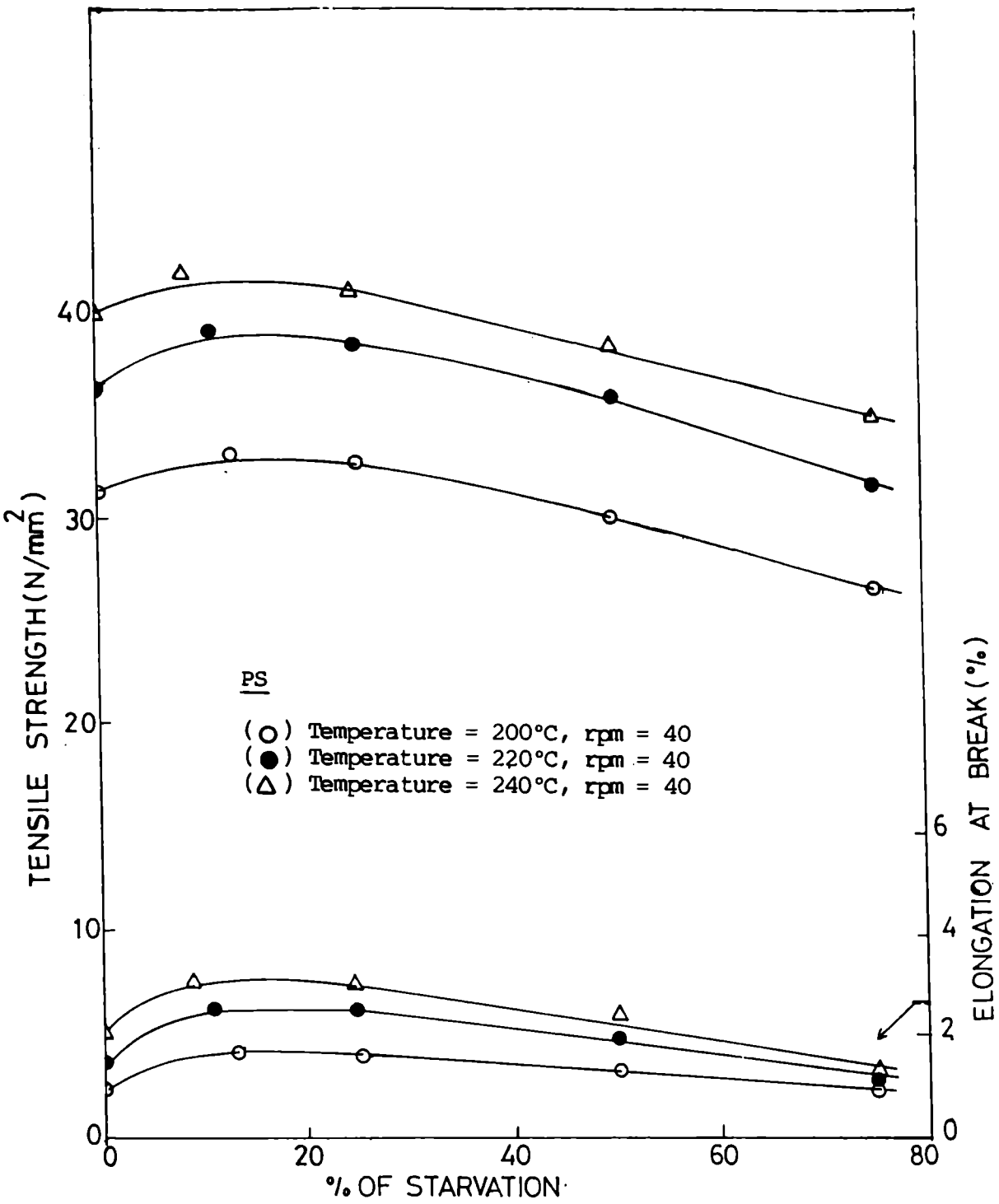


Fig.5.14: Variation of tensile strength and elongation at break of PS with percentage of starvation at different temperatures.

the extrudates.[22-24] Moreover, properties of polymers depend less on pressure than on temperature.[23]

Table 5.2 shows the temperature and flow rate fluctuations of LDPE at different starvation levels (i.e., 0%, 10%, 25%, 50% and 75%) at an rpm of 40 and at temperature of 180°C. The temperature fluctuations are pronounced in the flood feeding (i.e., starvation of zero), force feeding levels and at higher starvation levels due to varying viscous heat generation. In the case of flow rate also, fluctuations are greater in the flood feeding, force feeding levels and again at higher levels of starvation. These greater fluctuations affect the quality of the extrudate because they affect the melting and mixing process taking place in the extruder screw channel.[24] D.P.Isherwood et al.[7] showed that die pressure fluctuations also get reduced at low levels of starvation of up to 10%. So minimization of the amplitudes fluctuations of extrusion variables depends on the ability of the screw to melt the polymer efficiently and then to mix it thoroughly.

Table 5.3 shows the temperature and flow rate fluctuations of PS at different starvation levels at an rpm of 80 and a temperature of 220°C. As in the case of LDPE, the temperature and flow rate fluctuations are more in the flood feeding, force feeding levels, and at higher starvation levels.

Table 5.2: Fluctuations of temperature and flow rate in the extrusions of LDPE at 1 minute intervals

Rpm	% Starvation	Temperature °C				Flow rate (mg/min)
		Set	Actual			
			Die	Zone I	Zone II	
40	75	180	179	183	182	2846
			180	178	183	3051
			182	177	179	5115
			182	179	182	4200
			181	182	181	3615
,,	50	180	180	184	182	7235
			179	182	179	5416
			181	181	180	8930
			180	183	182	6195
			182	180	181	9210
,,	25	180	180	182	181	10800
			180	180	181	10295
			179	181	182	10110
			181	180	180	12413
			179	181	182	10110
			181	180	180	12413
			180	181	179	11364
,,	10	180	180	181	180	12915
			180	180	181	12610
			179	179	180	12400
			180	182	179	13315
			180	180	180	13801
,,	0 (Flood feeding)	180	179	182	181	13625
			180	179	182	13994
			182	177	179	15840
			180	181	180	14320
			181	182	182	14845
,,	Force feeding	180	178	185	183	15110
			179	180	177	18325
			178	184	182	17436
			180	182	181	19220
			181	183	180	21365

Table 5.3 Fluctuationsof temperature and flow rate in the extrusion of PS at 1 minute intervals

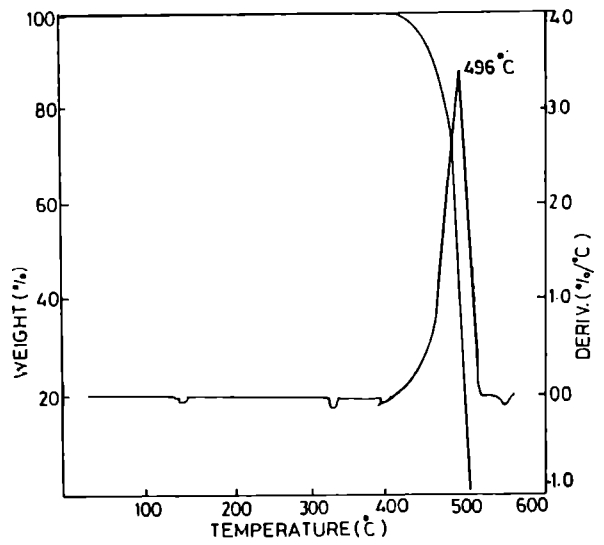
Rpm	% starvation	Temperature°C				Flow rate (mg/min)
		Set	Actual			
			Die	Zone I	Zone II	
80	75	220	222	225	222	8800
			222	222	223	8240
			220	218	221	6415
			221	220	219	7242
			219	221	220	5950
,,	50	220	221	223	221	15325
			220	218	223	14290
			222	220	220	16384
			220	219	222	12605
			221	220	221	14470
,,	25	220	220	222	221	22945
			220	219	222	22481
			219	218	220	20850
			219	219	220	20515
			219	220	218	20340
,,	10	220	220	222	220	26850
			220	220	218	25912
			220	221	219	25720
			219	218	218	25614
			219	220	219	25295
,,	0 (Flood feeding)	220	220	223	221	29985
			218	218	219	27890
			219	219	221	28925
			220	223	218	29457
			219	220	220	28400
,,	Force feeding	220	223	226	224	38010
			221	219	220	36370
			220	216	221	35414
			222	220	222	37215
			220	222	218	34001

5.3.5 Thermogravimetric analysis

TGA traces of the starve fed (low level of starvation), flood fed and force fed, samples of LDPE are shown in the Figs.5.15–5.17 and Figs.5.18–5.20 show the TGA traces of the starve fed, flood fed and force fed samples of PS. The traces show that the starved sample has higher transition temperature than the flood fed and force fed samples. This shows that the starve fed compound is more thermally stable than the flood fed and the force fed compounds. This behavior results from the more uniform temperature and shear history to which the compound was subjected to in starve feeding than in normal feeding. The higher difference in the transition temperature of starve fed and flood fed samples of LDPE shows the higher thermal stability acquired by the starve fed compound of LDPE than that of PS. This further shows that the effect of starve feeding is more pronounced in crystalline polymers like LDPE than that in amorphous polymers like PS.

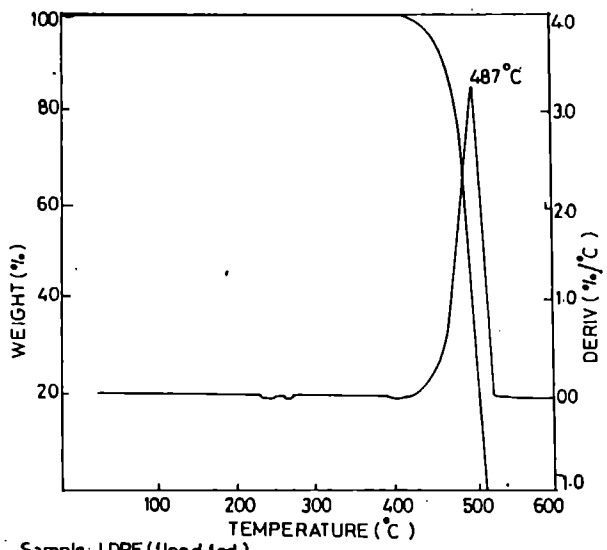
5.3.6 Density and crystallinity

Table 5.4 shows the variation in density of selected samples of LDPE and PS. It may be observed that the samples, which give the maximum properties, show the maximum density indicating that there can be minor variations in the percentage crystallinity[25] with the feeding rate. LDPE, being a crystalline plastic, shows appreciable variations, while PS, being an amorphous plastic, shows only minor variations. In



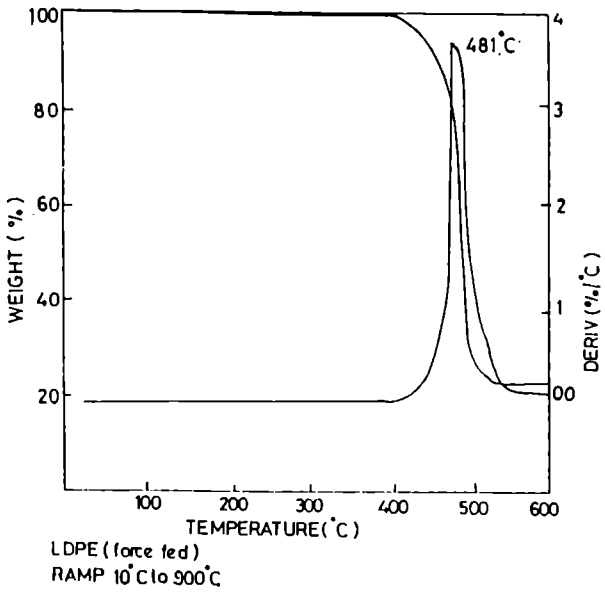
Sample: LDPE (starve fed)
Method : Ramp 10°C to 900°C

Fig.5.15
Starve fed



Sample: LDPE (flood fed)
Method: Ramp 10°C to 900°C

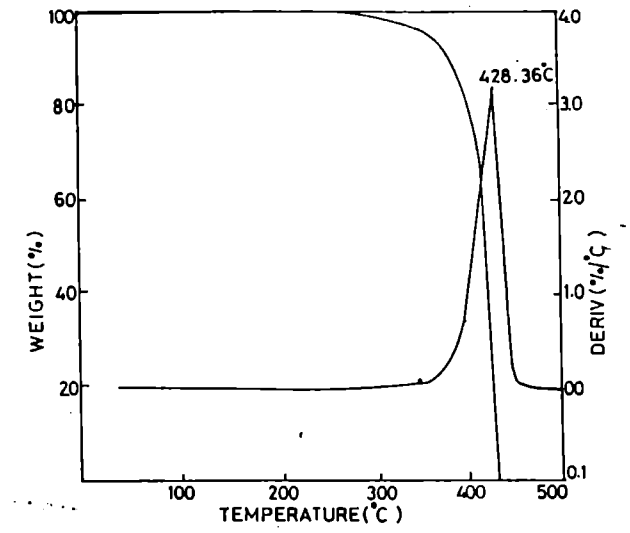
Fig.5.16
Flood fed



LDPE (force fed)
RAMP 10°C to 900°C

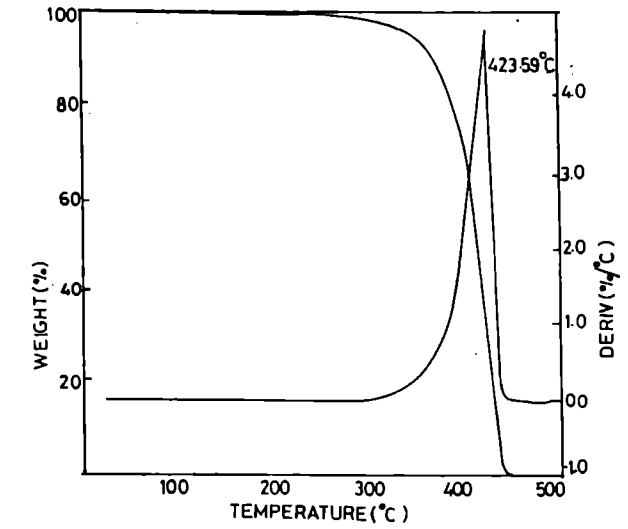
Fig.5.17
Force fed

TGA Traces of LDPE



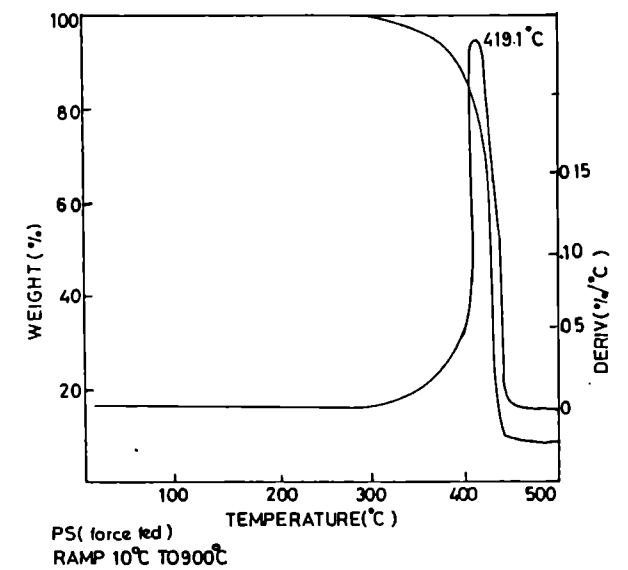
Sample: PS (starve fed)
Method: Ramp 10°C to 900°C

Fig.5.18
Starve fed



Sample: PS (flood fed)
Method: Ramp 10°C to 900°C

Fig.5.19
Flood fed



PS(force fed)
RAMP 10°C TO900°C

Fig.5.20
Force fed

TGA Traces of PS

Table 5.4: Variation of density and Brookfield viscosity of extruded LDPE and PS with percentatge of starvation

	Feeding rate (mg/min)	% Starvation	Density (g/cc)	Viscosity (centipoise)
LDPE extruded at 40 rpm and 180°C	3600	75	0.905	202
	7200	50	0.908	225
	10800	25	0.916	254
	12960	10	0.927	285
	14400	0 (Flood feeding)	0.905	231
	18000	Force feeding	0.903	206
PS extruded at 80 rpm and 220°C	7200	75	1.071	520
	14400	50	1.078	542
	21600	25	1.086	555
	25920	10	1.088	578
	28800	0 (Flood feeding)	1.070	514
	36000	Force feeding	1.067	503

the case of PS, the variation in density may be solely due to uniform melting and shearing resulting in uniform compaction.

5.3.7 Brookfield viscosity

In many of the polymer processing operations such as extrusion and injection moulding, the molten polymer experiences relatively high shear rate and hence a non-uniform heat generation. This may result in polymer degradation. Melt/solution viscosity may be used to monitor the degradation in polymers.[26-28]

Table 5.4 shows the viscosity of the solutions of extrudates of LDPE and PS at different feeding rates. The maximum viscosity is observed at the feeding rate at which the maximum extrudate properties are obtained at a low level of starvation. At the flood feeding and force feeding points mechanical breakdown is found to be higher due to non-uniform shear induced heating. The simultaneous increase in tensile strength and elongation at break of the samples of PS and LDPE at this particular lower level of starvation may be due to comparatively less mechanical breakdown which results in higher viscosity values.[5,29]

5.3.8 DSC curves

Figures 5.21–5.23 show the DSC curves of the starve fed (low level of starvation at which maximum properties are observed), flood fed and force fed samples of LDPE and Figs. 5.24–5.26, the respective DSC curves

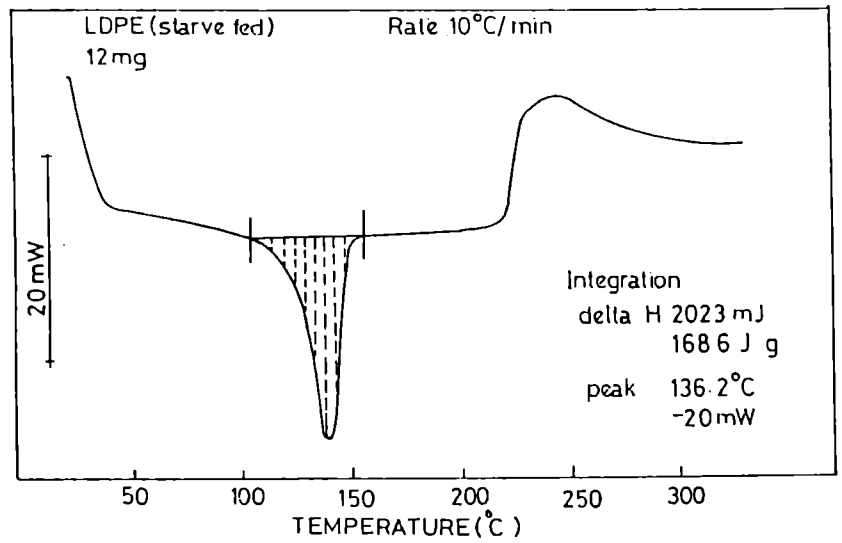


Fig.5.21
Starve fed

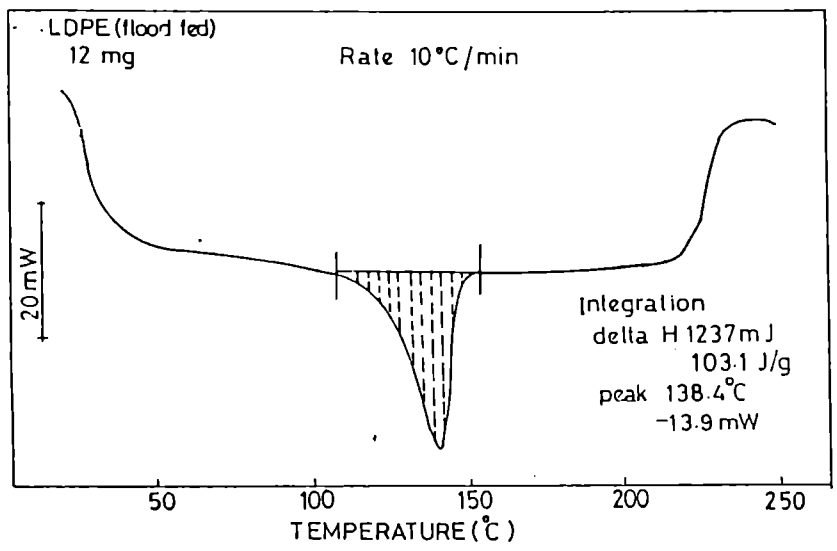


Fig.5.22
Flood fed

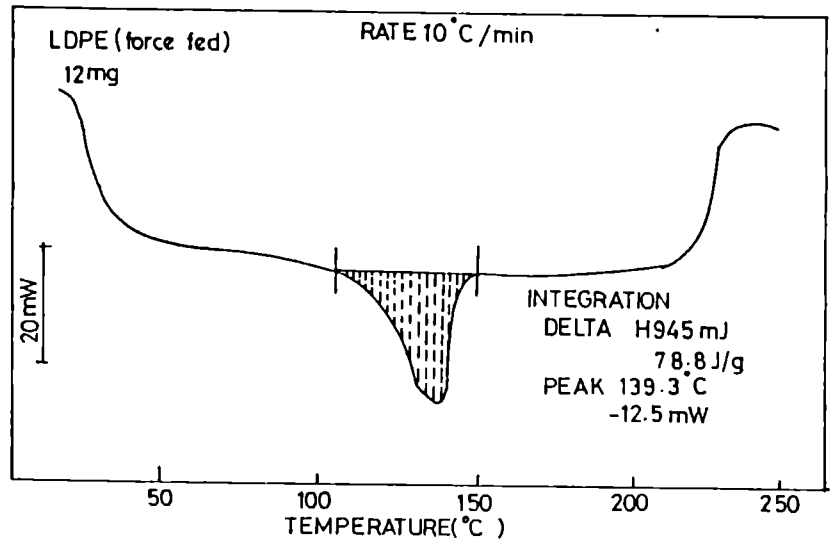


Fig.5.23
Force fed

DSC curves of LDPE

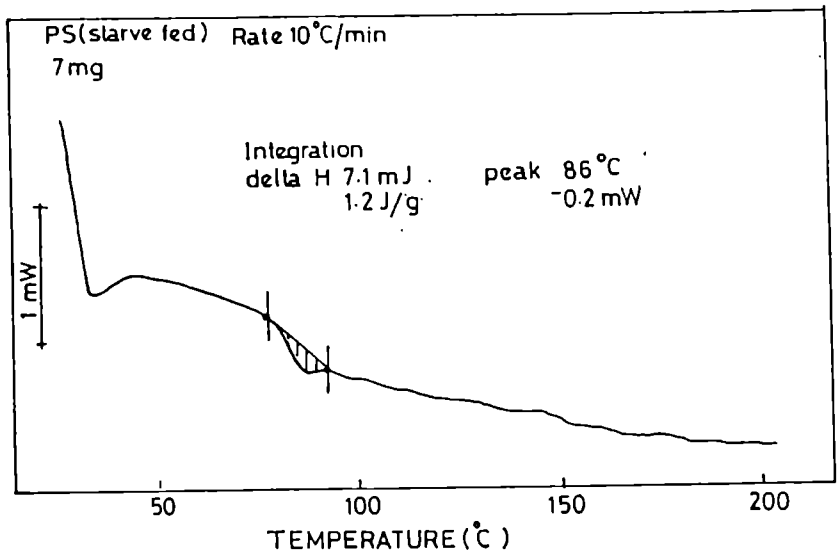


Fig.5.24
Starve fed

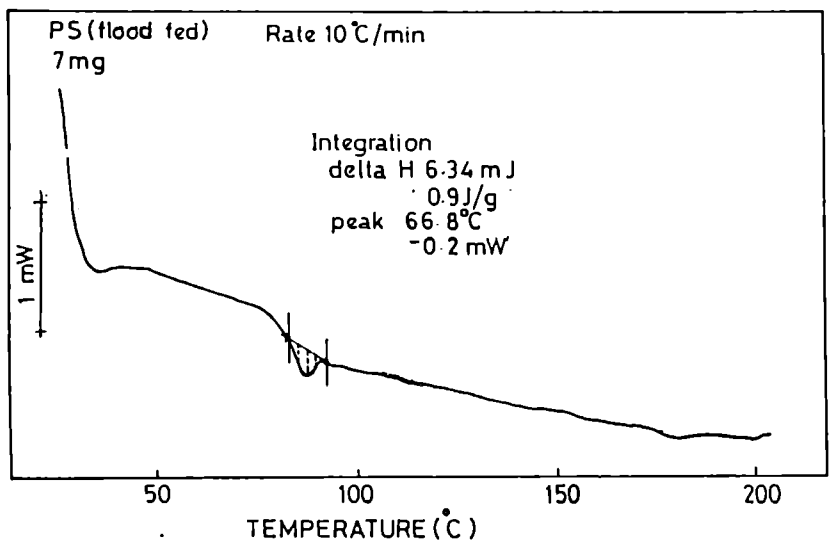


Fig.5.25
Flood fed

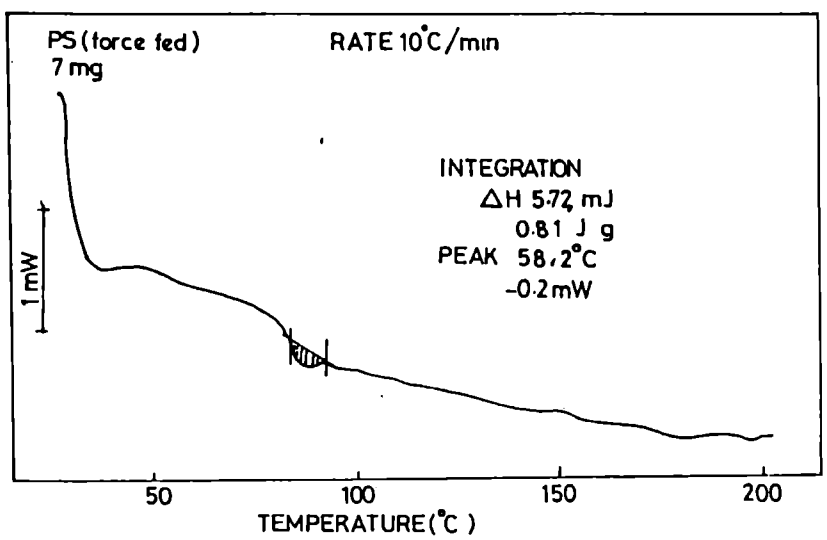


Fig.5.26
Force fed

DSC curves of PS

of the corresponding samples of PS. It is observed that degree of crystallinity in the starve fed sample of LDPE is higher than that of the flood fed and force fed samples as seen from the ΔH value which is higher[30-32] for the starve fed sample. In the case of PS, there is only marginal change in ΔH values of the starve fed, flood fed and force fed samples.

5.3.9 Optical microscopic studies

Optical microscopy was used for the study of internal flaws such as cracks, crazes, and shear bands which can be seen in transparent materials and so cause stress whitening which occurs in the plastic zone of the polymers.[33] Moreover it can be used to study the crystal structure and inter–particle bonding in polymers.[34,35]

The extrudate surface characteristics of starve fed, flood fed and force fed samples of LDPE are shown in Figs.5.27–5.29 respectively and that of PS are shown in Figs.5.30–5.32 respectively. In the case of LDPE, the starve fed surface of the sample shows more uniform arrangement of lamellar crystals, than those in the flood fed and force fed surfaces of the LDPE samples and these lamellar crystals are normal to the stress direction arranged in fibrillar units parallel to the stress as observed in an extruded LDPE sheet. In the case of PS it is observed that in the starve fed compounds, there is more uniform relative arrangement of particles and this may be due to higher amount of inter-particle bonding. So, the

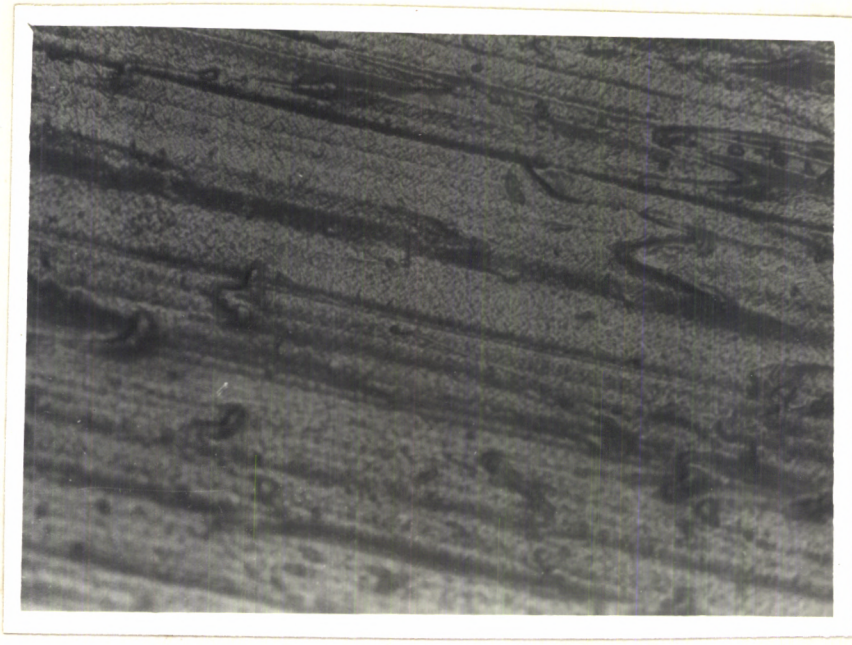


Fig.5.27 Starve fed

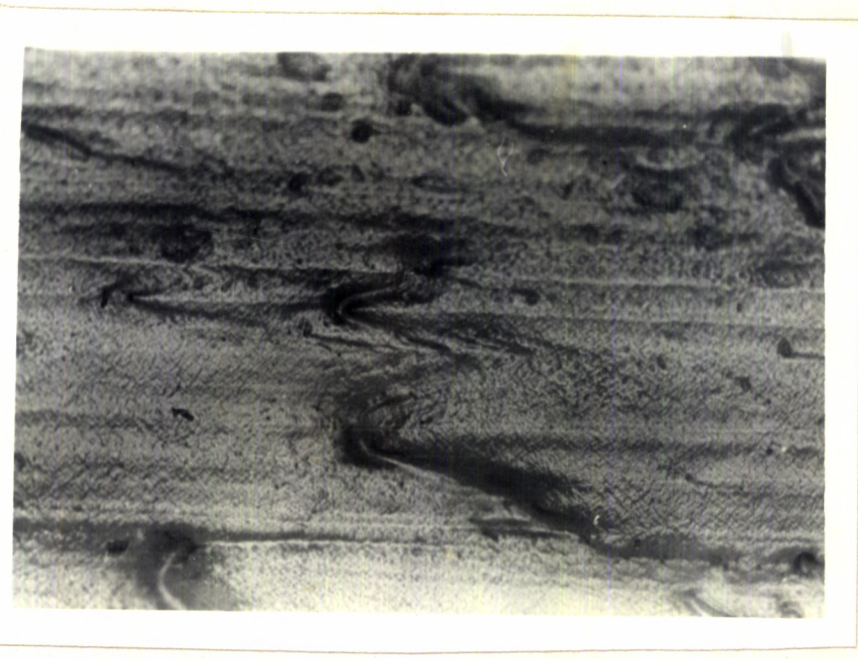


Fig.5.28 Flood fed

Optical micrographs of the surfaces of LDPE extrudates.

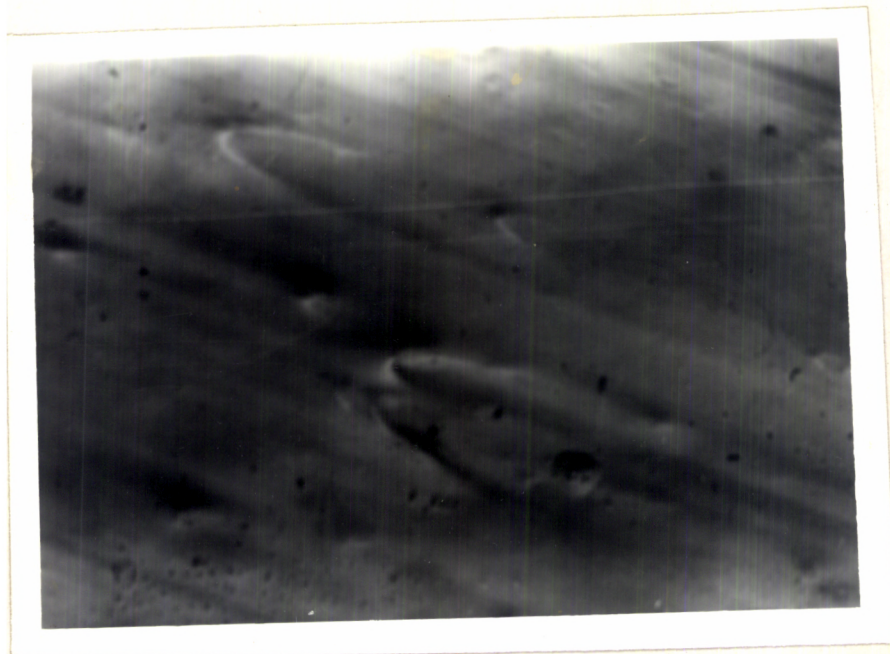


Fig.5.29 Force fed

Optical micrograph of the surface of the LDPE extrudate.

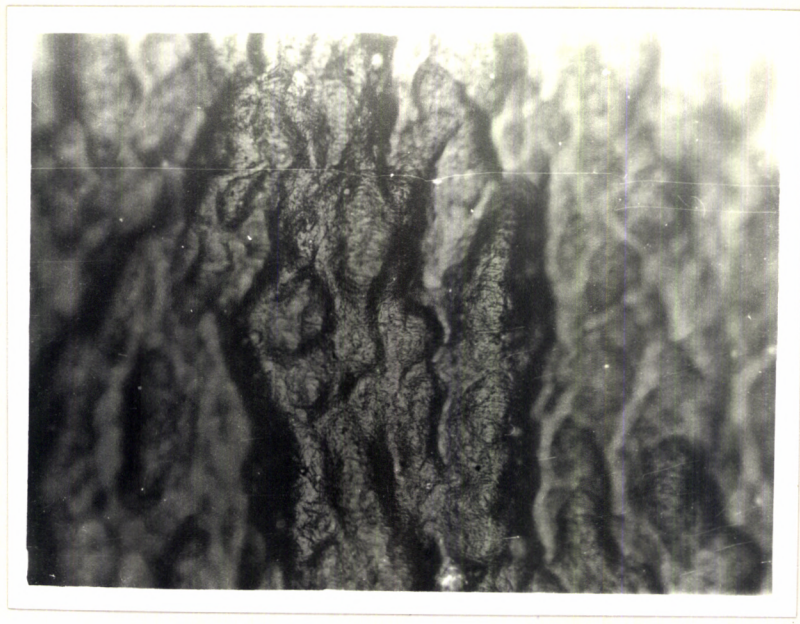


Fig.5.30 Starve fed

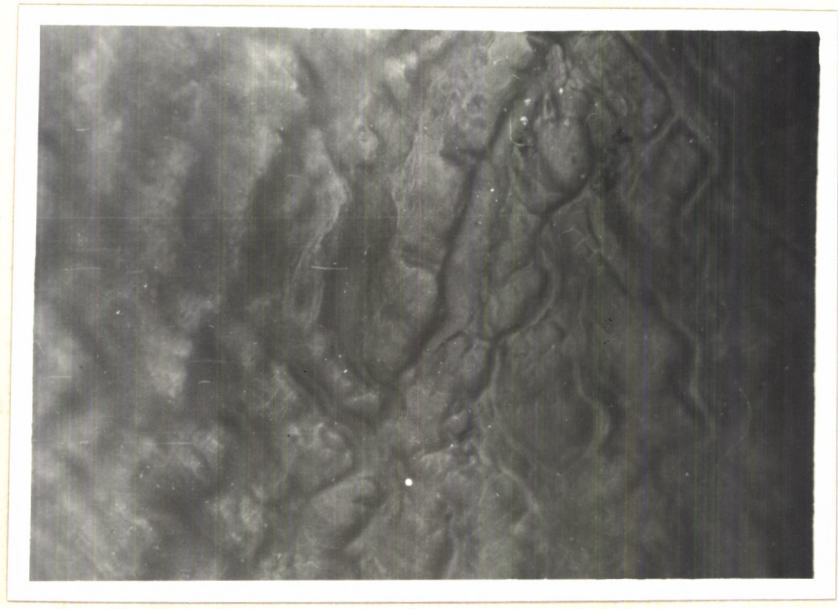


Fig.5.31 Flood fed

Optical micrographs of the surfaces of the PS extrudate.

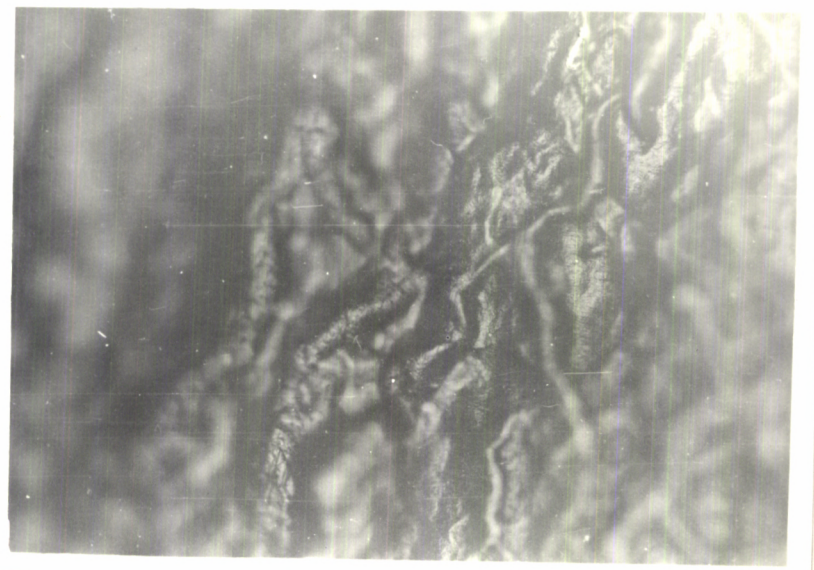


Fig.5.32 Force fed

Optical micrograph of the surface of PS extrudate

more uniform crystalline nature in the starve fed compound of LDPE and the higher amount of inter-particle bonding in the starve fed compound of PS may be possibly due to more uniform temperature distribution.

5.3.10 SEM studies and mechanical properties

Figures 5.33–5.35 show the SEM photographs of the tensile fracture surfaces of the respective starve fed, flood fed and force fed samples of LDPE. A more uniform fibrillar crystalline morphology[36,37] and more increase in inter-crystalline connections[38] are observed in the starve fed sample which shows maximum technical properties than that the flood fed and force fed samples.

Figures 5.36–5.38 show the SEM photographs of the tensile fracture surfaces of the starve fed, flood fed, and force fed samples of PS respectively. The figures express a plastic deformation due to crazing and shear banding in an amorphous polymer like PS.[39] Shear banding is a local deformation to the stress direction, which results in a high degree of chain orientation and is more pronounced in the starve fed sample leading to less mechanical breakdown.[33,40] So starved compound may get more orientation and less degradation which results in more tensile properties.

5.4 CONCLUSIONS

The study shows that the feeding rate in respect of the single screw extrusion of a semicrystalline plastic material like LDPE and an

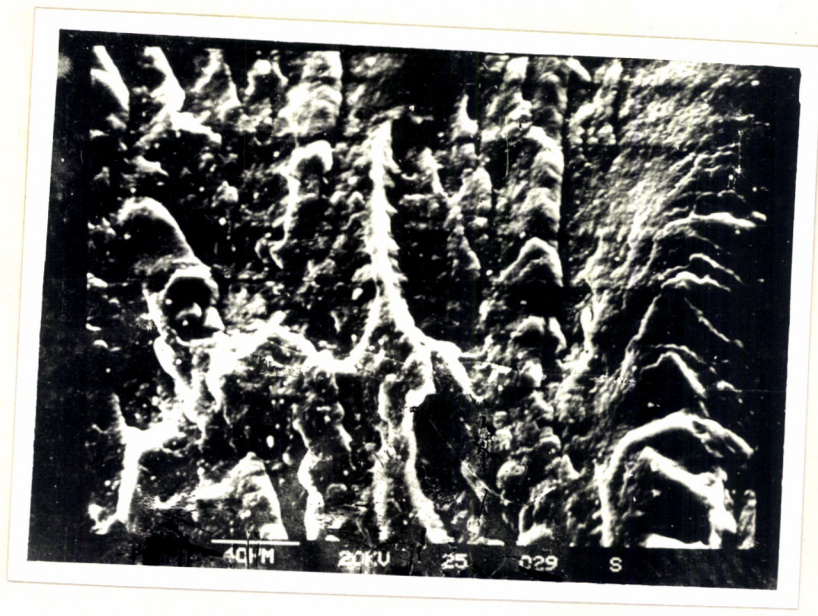


Fig.5.33 Starve fed

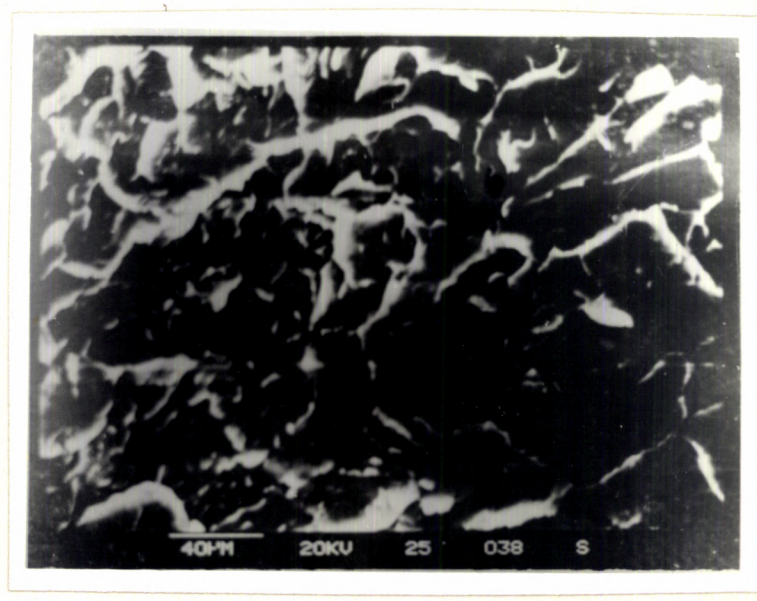


Fig.5.34 Flood fed

SEM photographs of the tensile fracture surfaces of LDPE

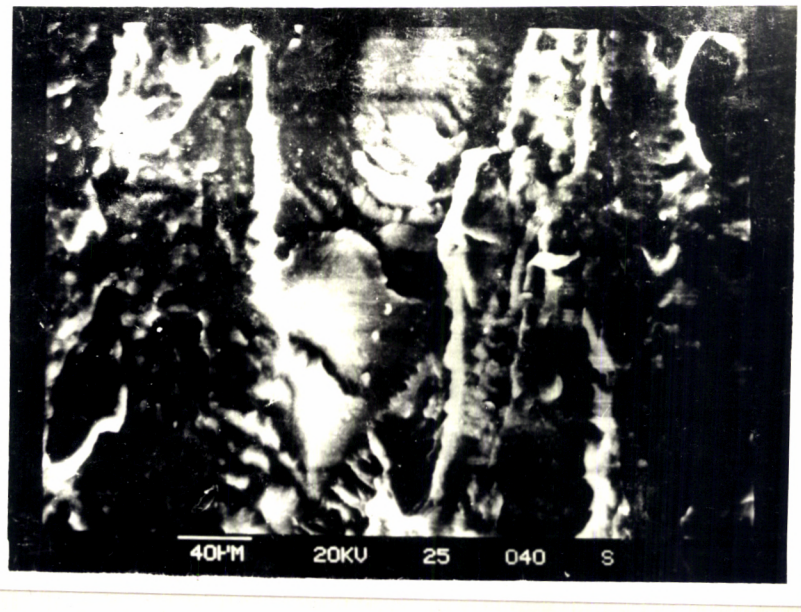


Fig.5.35 Force fed

SEM photograph of the tensile fracture surface of LDPE

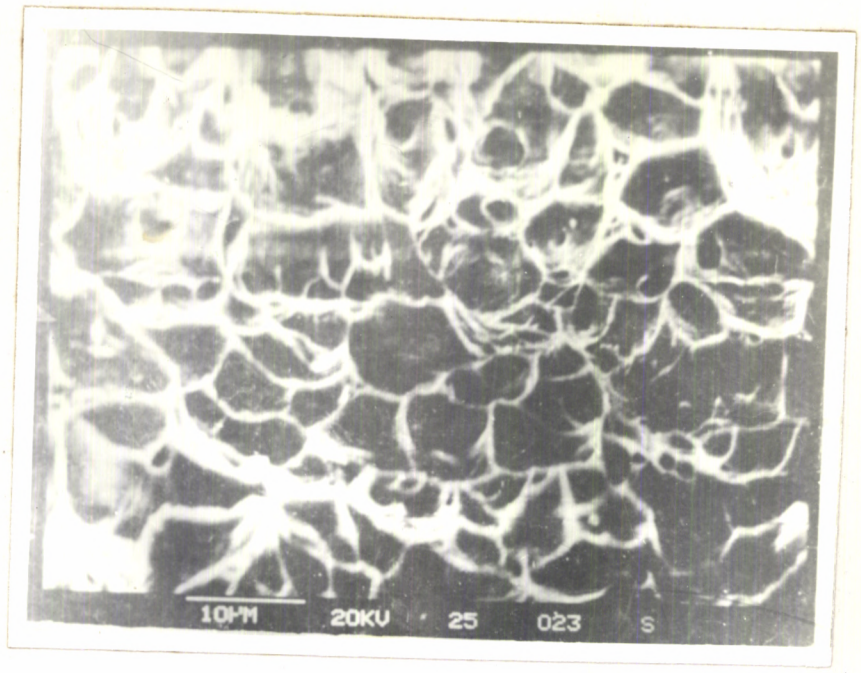


Fig.5.36 Starve fed

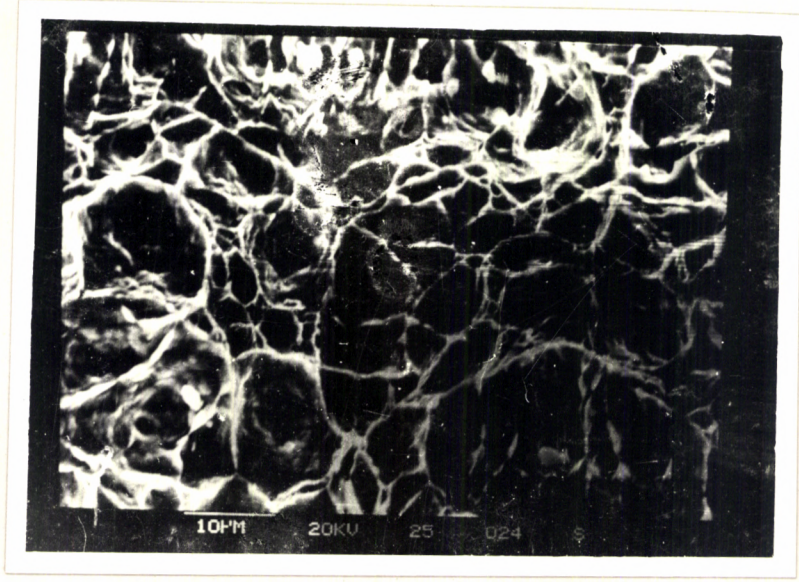


Fig.5.37 Flood fed

SEM photographs of the tensile fracture surfaces of PS.

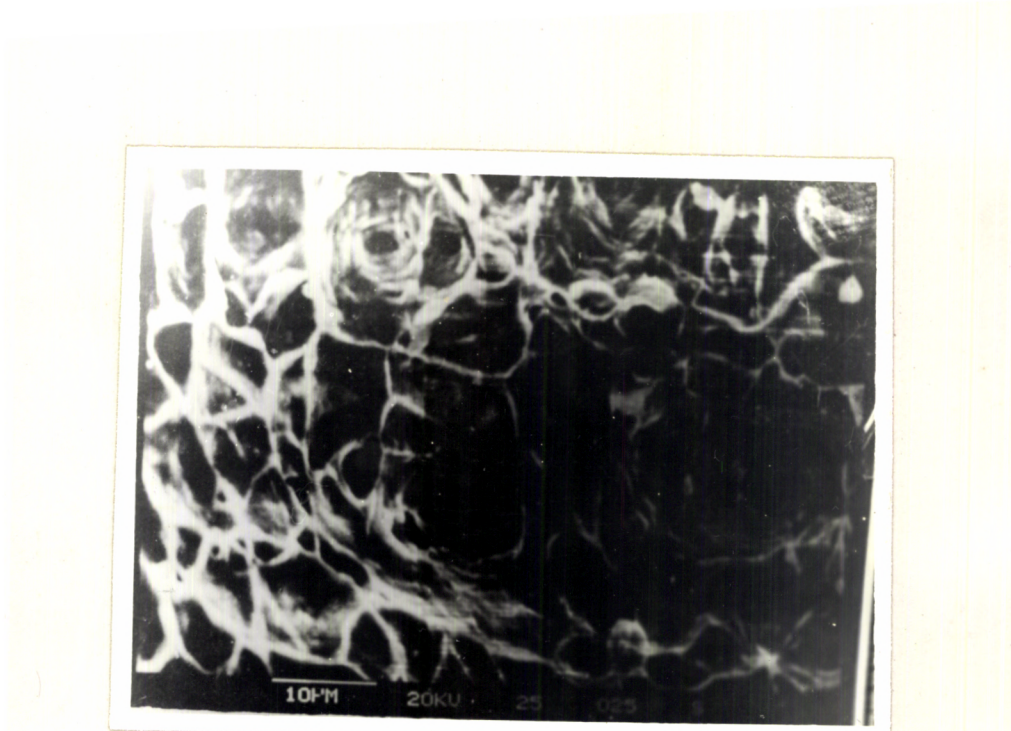


Fig.5.38 Force fed

SEM photograph of the tensile fracture surface of PS.

amorphous plastic material like PS affects their mechanical properties. The following conclusions can be drawn from the study.

1. For a given screw, there is an optimum feeding rate in the starved region which results in maximum physical and technical properties of the extrudates.

2. Running the extruder at a slightly starved condition is a promising technique of obtaining maximum technical and physical properties in addition to running the extruder at a lower torque.

3. In the case of LDPE, better homogeneity in melting and shearing gives a more favourable microstructure while in the case of PS homogeneity in temperature and shearing gives a favourable compaction.

REFERENCES

1. A.V. Shenoy and D.R.Saini, Polym. Plast. Technol. Eng., 23(1), 37 (1984).
2. R.W.Nelson, D.Chan, B.Yang and L.James Lee, Polym. Eng. & Sci., 26(2), 144 (1986).
3. J.H.Prichard and K.F. Wsissbrun, J. Appl. Polym. Sci., 13, 233-9 (1969).
4. L.A.Rudin and H.P.Schreiber, Polym. Eng. Sci., 23, 422-30 (1983).
5. P.J.Joseph Francis, Rani Joseph and K.E.George, Intern. J. Polymeric Mater., 38, 66 (1997).
6. G.Menges and J.Miller, Plastverarbeiton, 21, 305 (1970).
7. D.P.Isherwood, R.N.Pieris and D.Valamonte, Plast. Rubb. Proc. & Appl. 4, 257–260 (1984).
8. P.J.J.Francis, R.Joseph and K.E.George, Kautschauk Gummi Kunststoffe, 50 (10), 704 (1997).
9. P.J.Joseph Francis, Rani Joseph and K.E.George, J. Elast. & Plast., 29, 149 (1997).
10. D.P.Isherwood, R.N.Pieris, J.Kassataly and D.Valamonte, "Some Experiments on Metered Starve Feeding in the Extrusion Process", ASME Design and Production Engineering Conferences, Washington, pp.135–144 (1982).
11. F.W.Billmeyer, Jr., "Text Book of Polymer Science", (3rd edn.), John Wiley and Sons Inc., 17, 478–479 (1984).

12. B.Elbirli, J.T.Lindt, S.R.Gottgetreu and S.M.Baba, Polym. Eng. Sci., 23(2), 86 (1983).

13. G.Pinto and F.Tadmor, Polym. Eng. Sci., 10, 279 (1970).

14. D.M.Bigg and S.Middleman, Ind. Eng. Chem. Fundam., 13, 66 (1974).

15. K.Riess and W.Meskat, Chem. Ing. Tech., 23, 205 (1951).

16. W.Meskat, Kunststoffe, 41, 417 (1951).

17. H.J.Zamodits and J.R.A.Pearson, Trans. Soc. Rheology, 13, 357 (1969).

18. K.B.Abbas and R.S.Porter, J. Appl. Polym. Sci., 20, 1301-1312 (1976).

19. L.R.Whitlock and R.S.Porter, J. Polym. Sci., Part A-2, 10, 877-886 (1972).

20. G.Schenkel, Kunststoffe, 60, 52 (1970).

21. M.J.Stevens, "Extruder Principles and Operation", Elsevier, London (1985).

22. S.Anders, Plaste Kautsch, 27, 385 (1980).

23. Z.Tadmor and I.Klein, "Engineering Principles of Plasticating Extrusion", Van Nostrand Reinhold, New York, Chap.9 (1970).

24. Krzysztoff Wilczynski, "Evaluating Screw Performance in Extrusions", Nicholas P.Cheneminisof (Ed.), Marcel Deckker Inc., N.Y. , Chap.3 (1983).

25. L.Mandelkern, "Crystallization of Polymers", Mc-Graw-Hill, New York, Chap.8 (1964).

26. D.R.Saini and A.V.Shenoy, J. Elast. Plast., 17, 189-217 (1985).

27. N.G.Kumar, J. Polym. Sci., Rev., 15, 255-325 (1980).

28. Z.Komblowski and Turzecki, Rheol. Acta, 22, 34-40 (1983).

29. P.J.Joseph Francis, Rani Joseph and K.E.George, Iranian Polymer Journal, 86(1), 24 (1997).

30. M.J.O'neil, Anal. Chem., 38, 13–31 (1966).

31. J.M.Widmaier and G.C.Meyer, Macro Molecules, 14, 450 (1981), Rubb. Chem. Technol., 54(5), 940 (1951).

32. K.C.Frisch, D.Klemprer, S.Migdal, H.L.Frisch and H.Chiradella, Polym. Eng. Sci., 14, 76 (1974).

33. Linda C.Sawyer and David T.Grubb, "Polymer Microscopy", (2nd edn.), Chapman & Hall, London, Chap.4 (1996).

34. A.Keller and M.J.Machin, J. Macromol. Sci. Phys., B, 41 (1967).

35. R.S.Stein, J.Polym. Sci., 24, 383 (1957).

36. D.C.Bassett, C.R.C Crit. Rev. Solid State Mater. Sci., 12 (2), 97 (1984).

37. H.D.Keith and F.J.Padden, J. Appl. Phys., 34, 2409 (1963).

38. A.E.Zachariades, T.Konamoto and R.S.Porter, J. Polym. Sci. Polym. Phy. Ed., 18, 575 (1980).

39. L.Engel, H.Klingele, G.W.Ehrenstein and H.Schaper, "An Atlas of Polymer Damage", Prentice Hall, New Jersey (1981).

40. D.T.Grubb, J.A.Oddell and A.Keller, J.Mater.Sci., 10, 1510 (1975).

CHAPTER 6

SUMMARY AND CONCLUSIONS

SUMMARY AND CONCLUSIONS

The primary aim of this study has been to investigate the effect of feeding rate on the mechanical properties of extrudates in the case of plastics and rubbers. The study was undertaken in the case of different elastomers (both gum and filled) such as (1) Natural rubber, (2) Styrene-butadiene rubber and (3) Butyl rubber and plastics such as (1) Low density polyethylene and (2) Polystyrene.

It was observed that the extrusion rate or feeding rate in a single screw extruder affects the mixing, melting and homogenizing actions and hence affects the properties of the extrudates. The extent of variation of properties with feeding rate depends on the nature of the elastomers/plastics. In the case of rubbers, the effect of the extrusion rate of the compounds persists even after their curing.

The effect of feeding rate on the technical properties of unfilled natural rubber, styrene butadiene rubber and butyl rubber vulcanizates is described in chapter 3. The studies were done on a rubber extruder attached to a Brabender plasticorder model PL 2000 with an L/D ratio of 10 and a compression ratio of 1 and provided with a feeding roll. The study shows that best technical properties of the rubber vulcanizates are obtained when the corresponding compound is extruded at a low level of

starvation. This means that depending on the elastomer and the rpm of the screw there is a particular feeding rate in the starve fed region which is the optimum feeding rate as far as technical properties of the vulcanizates are concerned. The reason for this effect is attributed to the better mixing and homogeneity in the starved region than in flood fed region. Natural rubber vulcanizates show the maximum change in properties with feeding rate compared to SBR and IIR vulcanizates. The properties of the vulcanizates of all the three elastomers are found to increase with the extrusion temperature till a particular temperature, depending upon the elastomers, at which thermal degradation seems to make a serious deterioration in properties. The fluctuations in extrusion variables like temperature, flow rate etc. are also found to be minimum at the particular feeding rate at which best technical properties are obtained supporting the earlier proposition that better homogeneity is obtained at that feeding rate.

Studies conducted in the case of unfilled elastomers in chapter 3 were repeated for filled elastomers due to their commercial importance. As in the case of the gum elastomers, it was found that there is a particular feeding rate in the starve fed region which results in the best mechanical properties. The starve fed sample was also found to be more thermally stable from TGA studies. This fact further suggests that this compound was subjected to a more uniform temperature and shear. Brookfield viscosity of the solutions of starve fed extruded rubber

compounds were found to be higher than those of the flood fed or force fed samples indicating that mechanical degradations are less in the starve fed compounds due to lower shear and better thermal homogeneity. Further starve fed compounds also give rise to vulcanizates having a higher crosslink density. The carbon black dispersion in starve fed compounds is also found to be superior to that of flood fed compounds.

The effect of feeding rate on plastic extrudates form the contents of chapter 5. Extrusion studies were conducted on a laboratory extruder attached to a Brabender plasticorder model PL2000 with an L/D ratio of 25 and a compression ratio of 2 provided with a hopper for feeding. In the case of both a semicrystalline plastic LDPE and an amorphous plastic PS extrusion rate was found to affect the mechanical properties. As in the case of rubber extrusion, there is an optimum feeding rate in the starve fed region. The better temperature and shear homogeniety in the starve feeding give rise to increased crystallinity and density as shown by the DSC. As in the case of elastomers, shear break down during starved extrusion is also found to be only of a lesser degree than flood or force feeding. The SEM photographs of the tensile fracture surface of the samples indicate better homogeneity in the respective starve fed samples. Lower production rate is usually pointed out as one of the serious shortcomings of starve feeding. But the results of the present investigations indicate that in most cases the increase in mechanical properties can compensate the lower thicknesses or dimensions resulting

from starve feeding. Further the rpm of the screw may be increased still maintaining a low starving condition to enhance the production rate.

LIST OF PUBLICATIONS FROM THIS WORK

1. "Starved extrusion for the improvement of mechanical properties of rubber vulcanizates", Journal of Elastomers and Plastics, 29(2), 148–162 (1997).

2. "Significance of feeding rate in the extrusion of filled and gum IIR vulcanizates", International Journal of Polymeric Materials, 38, 65–78 (1997).

3. "Effect of starved feeding on rubber extrudate properties", Kautschuk Gummi Kunststoffe, 50(10), 704–709 (1997).

4. "Starved feeding for improving the mechanical properties of styrene-butadiene rubber vulcanizates", Iranian Polymer Journal, 6(1), 19–26 (1997).

5. "Effect of feeding rate on plastic extrudates", International Journal of Polymeric Materials (in Press).

6. "Starved extrusion for the improvement of mechanical properties of gum NR vulcanizates", Paper presented at the

International Conference on Macro-Molecules, VSSC, Thiruvananthapuram (January 1995).

7. "Feeding rate as an important parameter in the extrusion of filled NR vulcanizates", Paper presented at the National Conference on Polymer Technology, IIT, Kharagpur (13th January 1996).

8. "Effect of feeding rate on rubber extrusion", Paper presented at 8th Kerala Science Congress, Kochi (27–29 January 1996).