# STATIC AND DYNAMIC MECHANICAL PROPERTIES OF (BAUXITE, AND CARBON BLACK) FILLED SBR VULCANIZATES: EFFECTS OF FILLER SURFACE MODIFICATION ON PROPERTIES

A Ph.D. Thesis
in Chemistry
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by
İlhan Ülkem
July, 1990

......TO MY MOTHER AND FATHER......

Approval of the Graduate School of Natural and Applied Sciences

R. Sene

Prof.Dr.Alpay Ankara

Director

I certify that this thesis satisfies all the requirements as a thesis for the degree of Doctor of Philosophy in Chemistry.

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Assoc. Prof. Dr. İnci Gökmen

Vice Chairman of the Department

We certify that we have read this thesis and that in our opinion it is fully adequate, in scope and quality, as a thesis for the degree of Doctor of Philosophy in Chemistry.

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# STATIC AND DYNAMIC MECHANICAL PROPERTIES OF (BAUXITE, AND CARBON BLACK) FILLED SBR VULCANIZATES:
## EFFECTS OF FILLER SURFACE MODIFICATION ON PROPERTIES

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## ABSTRACT

A research was conducted to investigate relationships between mechanical properties and surface properties of the fillers used in SBR vulcanizates.

Surface modification of fillers were realized by plasma polymerization of styrene and butadiene at room temperature and surface area measurements were done by mercury porosimetry, nitrogen adsorption and sedimentation techniques. It was observed that surface area changes are negligible for plasma polymerized polystyrene coated bauxite and carbon black whereas they are 40.9 % and 7.6 % for plasma polymerized polybutadiene coated bauxite and carbon black, respectively, Solvent casting technique was also used to coat the surface of some fillers and it became possible to see the effect of coating thickness on the mechanical properties of the vulcanizates.

The existence of possible selective surface interactions was investigated by dynamic mechanical analysis and they were verified by the observation of shifted values for Tg' s due to plasma modified surfaces of fillers.

SEM technique was used to investigate the fracture surfaces of the vulcanizates. From the SEM photographs different surface patterns were observed due to different kinds of coatings.

Elemental analysis technique was applied to the plasma polymerized polystyrene and plasma polymerized polybutadiene coated bauxite samples for the detection of trace amounts of carbon, although the thickness of coatings was of angstrom scale. ATR-FTIR technique was also used to investigate the surfaces of the vulcanizates for which uncoated and coated carbon black were used as fillers.

Mechanical properties such as tensile strength and % elongation were measured with Instron Tensile Testing Machine and hardness measurements were done with an automatic constant weight Shore A durometer. It was observed that tensile strength and % elongation increase for plasma polystyrene coated samples and they decrease for plasma polybutadiene coated samples. It was also observed from the hardness measurements that plasma polystyrene coated fillers are making the vulcanizates softer while plasma polybutadiene coatings are making them harder.

Minimum viscosity, scorch time and cure state of the coated and uncoated filler used compounds were also studied by a rheometer.

Finally a mathematical relationship was tried to be found to estimate the tensile strength and hardness values of the vulcanizates.

**Key Words:** Plasma polymerization, plasma coating, filler, reinforcing filler, bauxite, carbon black, SBR, mechanical properties, dynamic mechanical properties, surface modification.

**Science Code** : 405.04.02

# BOKSİT VE KARBON SİYAHI DOLGULU SBR VULKANİZATLARINDA STATİK VE DİNAMİK MEKANİK ÖZELLİKLER: DOLGU MADDESİ YÜZEYİ MODİFİKASYONUNUN ÖZELLİKLER ÜZERİNDEKİ ETKİSİ

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## ÖZET

SBR vulkanizatlarında kullanılan dolgu maddelerinin yüzey özellikleri ile mekanik özellikleri arasındaki ilişkileri incelemek üzere bir çalışma gerçekleştirilmiştir.

Dolgu maddelerinin yüzey modifikasyonu stiren ve bütadien'in oda sıcaklığında plazma polimerizasyonu ile yapılmış olup yüzey ölçümleri cıva porozimetresi, azot absorpsiyonu ve sedimentasyon teknikleri ile sağlanmıştır. Plazma polistiren kaplı boksit ve karbon siyahının yüzey alanları pek değişmezken plazma polibütadien kaplı boksit ve karbon siyahının yüzey alanlarının sırası ile %40.9 ve %7.6 azaldığı gözlenmiştir. Bazı dolgu maddelerinin yüzeyleri çözeltiden çözgenin buharlaştırılması ile

yapılmış olup kaplama kalınlıklarının vulkanizatların mekanik özellikleri üzerindeki etkisi gözlenmeye çalışılmıştır.

Muhtemel tercihli yüzey etkileşimlerinin varlığı; dinamik mekanik analiz yöntemleri ile incelenerek plazma modifikasyonu ile ortaya çıkan Tg kaymaları ile saptanmıştır.

Örneklerin kopma yüzeyleri taramalı elektron mikroskopu ile incelenmiş olup değişik kaplamaların farklılığı yüzey dokusundaki değişikliklerle saptanmıştır.

Plazma polistiren ve polibütadien kaplı boksit örnekleri elementel analiz cihazı ile test edilmiş olup kaplamaların angström mertebesinde olmasına rağmen az miktarda karbon varlığı gözlenmiştir. Kaplanmamış ve kaplanmış karbon siyahı kullanılan örneklerin yüzeyleri ATR-FTIR Tekniği ile incelenmiştir.

Örneklerin kopma mukametleri, uzama yüzdeleri, ve sertlikleri Instron ve Shore A durometresi ile test edilmiş olup, plazma polistiren kaplı örneklerin daha mukavim ve daha yumuşak, plazma polibütedien kaplı örneklerin ise daha zayıf ve sert oldukları tesbit edilmiştir.

Kaplanmış ve kaplanmamış dolgu maddesi kullanılan örneklerin, minimum viskosite, yanma zamanı, ve pişmiş hal özellikleri reometre tekniği ile incelenmiştir.

Son olarak bütün bulgular bir matematik denklem yapımında kullanılarak kopma mukavemeti ve sertlik gibi özelliklerin hesap yöntemi ile tahmin edilebilinmesine çalışılmıştır.

**Anahtar kelimeler:** Plazma polimerizasyonu, plazma kaplama, dolgu maddesi, boksit, karbon siyahı, lastik, SBR, mekanik özellikler, dinamik-mekanik özellikler, yüzey modifikasyonu.

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# NOMENCLATURE

| | |
|---|---|
| SBR | Styrene Butadiene Rubber |
| pps | Plasma polystyrene |
| ppb | Plasma Polybutadiene |

# 1. INTRODUCTION

It has been known for a long time that additives wereused in polymers for several purposes. Although the use of them has started to minimize the production costs in the polymer industry at the beginning-as in the case of the other sectors-the subject (the use of additives) increased its importance excitingly not only because of the economic needs but also because this was the unique solution to get the desired properties of the polymeric products in most cases.

The following additives are used commonly in the polymer industry :[1].

-Fillers and other reinforcing agents,
-Stabilizers and antioxidants,
-Plasticizers,
-Coloring agents,
-Processing oils and lubricants,
-Catalysts,
-Antistatic additives,
-Fire retardents,
-Foaming agents, etc.

It is well known that among these additives the fillers especially the reinforcing ones have a very wide application area in the polymer industry. These reinforcing fillers such as carbon black are used in the rubber industry for a long time. Since that time; naturally, a lot of studies were conducted to understand the factors affecting the interaction between the fillers and rubber matrix.These factors may be classified as follows:[2].

(1)-EXTENSITY FACTOR : Total surface area of the filler,
(2)-INTENSITY FACTOR : Selectivity of the filler surface,
(3)-GEOMETRICAL FACTOR : Structure and porosity of the filler.

It is unfortunately for the science and fortunately for this thesis that the subject couldn`t be explained satisfactorily up to now and still needs further observations and explanations. For this purpose the first and the second factors mentioned above werestudied in this thesis.Some new interesting findings were obtained and they were modelled mathematically.

This thesis is composed of three basic chapters. In the first chapter background information about the subject will be summarized. The second chapter will present the experimental details and in the third chapter the results will be discussed and the conclusions will be mentioned.

## 2.1. GENERAL BACKGROUND

### 2.1.1. GENERAL INFORMATION ABOUT FILLERS

Fillers ; among the additives are the most important ones because in addition to reduce the cost, they also modify the properties of polymers. For example in brittle plastics, fibrous fillers are incorporated to confer impact strength. Other types of fillers are used to increase hardness, improve electrical properties, or alter the specific gravity. In flexible plastics the requirements for fillers are not so demanding, and hence they are mainly incorporated to reduce cost or to confer some particular property, such as , abrasion resistance, tear strength, tensile strength, impact strength, heat resistance, light fastness, good electrical properties, and fire and chemical resistance [3].

Fillers may be best classified according to their chemical and physical characteristics. They may be divided initially into organic and inorganic groups. Each of these two groups may be subdivided into fibrous and non-fibrous types; in addition, protein fillers are included in the organic group [4].

Many of the fillers may be further subdivided within any one group, depending on differences in physical characteristics such as particle-size distribution, particle size, particle shape, bulk density.

We can show the clasification of fillers in general as follows:[5].

| ORGANIC | | INORGANIC | |
|---|---|---|---|
| FIBROUS | NON-FIBROUS | FIBROUS | NON-FIBROUS |
| Cottonseed hulls | Carbon black | Asbestos | Silica |
| Sisal | Graphite | Glass fibre | Talc |
| Wood flour | Wallnut flour* | | Calcium silicate |
| Cotton flock | Coconut flour* | | Mica |
| Cotton linters | Cork dust | | Clays |
| Wood cellulose | | | Slate |
| | | | Kieselguhr |
| | | | Antimony trioxide |
| | | | Bauxite ($Al_2O_3$) |
| | | | Barium sulphate |
| | | | Calcium carbonate |

* Flour of the shell.

### 2.1.2. REINFORCING FILLERS

Sometimes the use of fillers in polymer industry conforms a very special pattern as in the case of rubber industry where fillers are mainly used for reinforcing purposes. This is because none of the known synthetic or natural rubbers can be used in the engineering applications while they are in their original form. So the fillers used in these applications are called reinforcing fillers and it should be mentioned at this point that carbon black is the most well known reinforcing filler especially in the rubber industry [6].

### 2.1.3. DIFFICULTIES DURING USAGE OF FILLERS

Although the fillers are playing a very important role in the polymer industry, unfortunately it is not so easy to use them directly. The difficulties arise because there exists a compatibility problem between the filler and polymeric matrix surfaces where a good adhesion is neededfor reinforcing purposes. There are three well-known reasons for this incompatibility. These are the filler particle size and its distribution, particle shape and structure ; and surface adhesion between the polymer and filler. The importance of these factors have been discussed finally in the "44th Annual Composites Institute Conference" [7] and filler suppliers and users were advised to develop technologies to improve particle size, shape and to avoid surface modification problems.

If the surface factor existing between the polymer and the filler is considered, an adhesion problem is faced.This problem may be due to both physical and chemical reasons. First of all there is a large surface need between polymer and filler which can be overcome more or less by using small particle size filler, but the structure and chemical nature of the surface are also important. For instance the polymer surface may be hydrophobic and the filler may be hydrophilic or there may be polarity and acidity problems.

More clearly and more specifically for rubbers; as far as carbon black is concerned, a summary of the following information would be useful:

The nature of the solid surface may be varying in a chemical sense, having different chemical groups, e.g., hydroxyl, metaloxide, carboxyl, quinone, or lactone groups,etc.[8,9]. In a physical sense, surfaces can be different in adsorptive capacity and energy of adsorption.

On the other hand chemical surface groups or different surface selectivities play an important role because they have also effects on the rate of cure with many vulcanizing systems [10].

As a summary it can easily be claimed that surface selectivity of the fillers (Intensity Factor) is a very important subject for reinforcing of elastomers as far as the chemical interaction for adhesion and vulcanization reaction kinetics are concerned. It should also be mentioned here that surface modification of fillers in rubber industry is lacking in the rubber technology because it is in contradiction with the continuity of the manufacturing processes (especially during tire manufacturing).

## 2.1.4. IMPORTANCE OF PLASMA POLYMERIZATION TECHNIQUE ON SURFACE MODIFICATION

There are several ways of surface modification to improve the adhesion. A polymeric chain may be grown on an initiation site on the surface in one approach, while in another small molecules, previously attached to the surface, are copolymerized with a monomer. In a third method, a polymeric chain is transferred to an active site on the supporting surface. For example Donnet and coworkers studied the thermal polymerization of styrene in the presence of carbon black in 1961 [11]. In 1969 Y.Minaura - M.Katano treated carbon black with butyllithium in the presence of tetramethyldiamine, to attach peripheral hydrogen to the black`s aromatic ring system and then they grafted polymer on the carbon black surface [12]. So basically by using coupling or decoupling agents, grafting of suitable polymers on to the base polymeric matrix or simply coating the filler surface it is possible to change the surface characteristics of the fillers. Among these, coating the filler surface directly is the most attractive one because just by creating a suitable coat to the filler it is possible to change the chemistry of the surface easily. But coating itself is a very popular research subject because to control the coat thickness and homogeneity while keeping the process continously flowing for production is not a simple task to manage, in addition to the problems of producing a non-durable coat in general.

A very simple surface treatment method for fillers is coating the surface with a polymer by solvent casting method from the solution which seems very easy but not in reality. Because first of all this technique needs high energy costs for solvent evaporation and there is a need of recycling the solvent which is an additional cost and process difficulty. On the other hand to keep such a process continuously flowing is not so easy. Finally and more importantly it is not possible to control the thickness of the coating even from the very dilute polymer solutions. So the thickness of this class of coatings is affecting the system adversely as far as the structure of the filler is concerned. As it was mentioned earlier fillers are different in shape and structure. These structure effects,namely the voids at the surface of filler, are very important for adhesion,(physically) because the polymer chains enter to these voids and it is a very suitable process to achieve the basic adhesion physically. But if these voids are covered with a coating that is thick enough this time this advantage of the filler structure will be lost. As a result the coating should be performed in such a way that while the surface of the filler is modified chemically its original structure pattern should not be disturbed.

It should be emphasized at this point that plasma polymerization technique is a very suitable method to get a very thin coat even in angstrom scale and by this way it is possible to change the surface nature without disturbing the original structure pattern.

### 2.1.5. DESCRIPTION AND THE USE OF PLASMA TECHNIQUE

Plasma can simply be defined as the 4th state of matter.There are several definitions available in literature for plasma. Some examples are given below:

The region in a discharge in gases in which the number of positive and negative ions are approximately equal [13].

A plasma is a partially ionized gas composed of ions,electrons and neutral species [14].

It is a state of matter that can be created by such diverse techniques as flames, electrical discharges, electron beams,lasers or nuclear fusion. The technique of most interest to plasma polymerization is the glow discharge, in which free electrons gain energy from an imposed electrical field and subsequently looses it through collisions with neutral molecules in the gas.The transfer of energy to gas molecules leads to the formation of a host of chemically reactive species,some of which become precursors to the plasma polymerization reaction.

The plasma created by a glow discharge possesses average electron energies in the range of 1-10 eV and electron densities of $10^9$-$10^{12}$/cc. In addition, the electron temperature $T_e$ of the plasma is not equal to the gas temperature $T_{gas}$ but has a $T_e/T_{gas}$ ratio of 10-100. It is therefore possible for plasma polymerization to proceed at near ambient temperatures in the presence of electrons to rupture covalent bonds in the gas molecules. Thus plasmas produced by the glow discharge are called non-equilibrium plasmas, in contradiction to equilibrium plasmas created by arcs or plasma jets where $T_e$=$T_{gas}$. Very high temperatures in these plasmas (in thousands of degrees Kelvin) render them unsuitable for plasma polymerizations, since polymers produced under these conditions will rapidly be degraded.

General applications of plasma technology can be summarized as follows: [15].

-Ion implantation,

-Microcirciut fabrication,

-Membranes,

-Biomedical applications,

-Optical applications,

-Plasma cleaning of metal surfaces,

-Plasma etching,

-Low-temperature ashing,

-Textile treatment,

-Plasma detoxification and air purification,

-Surface treatments.

Among these general application titles three interesting specific study will present the importance of surface treatment more clearly:

In one of the studies done by S. Kaplan and P. Rose, some of the frequently used polymers were treated with oxygen and ammonia plasmas.Later the effect of the surface treatment on adhesion was investigated by using epoxy and urethane based commercial adhesives [16].

In another study, plasma modified thermal carbon black was investigated for its usage as a packing material for gas chromatography [17].

Finally, in one study, mechanical properties of polymer composites were investigated by using plasma modified mica fillers [18].All these studies are very useful because they represent the importance of plasma technique on surface modification by introducing some great improvements on adhesion, selective seperation and mechanical properties. A simple schematic representation of the plasma system is given in Figure 1.

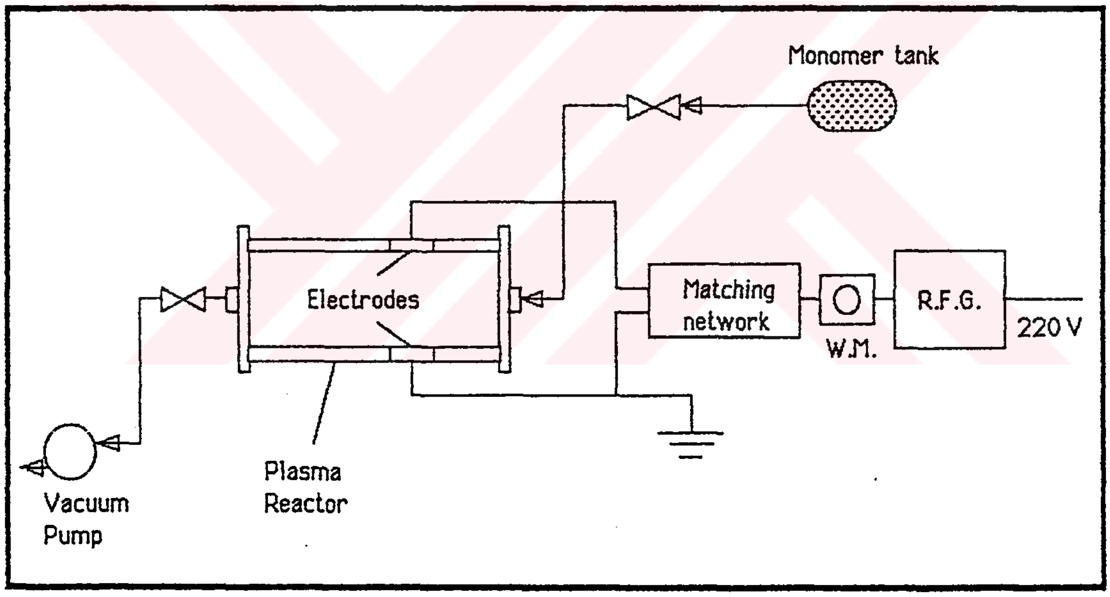


Figure 1. Schematic representation of a plasma system

## 2.2. COMPATIBILITY AND PRACTICAL PROPERTIES OF POLYMER BLENDS AND FILLED POLYMER SYSTEMS

### 2.2.1. HISTORY

The rubber, coatings, adhesives, thermoplastics, and thermoset plastics industries have a long history of blending polymers and using fillers to optimize the balance of properties for specific applications [19,20]. The thermoplastic industry approached to the concept much more cautiously and pessimistically over the past four decades. The ability of polymeric products (both blends and filled systems) to satisfy this need, converged in the succesful commercial high-impact polystyrene, ABS, rigid PVC, high-impact polypropylene, modified polyphenyleneoxide, carbonblack filled rubbers, and four families of thermoplastic elastomers during the 1940`s to the 1960`s. More recently, with growing activity in theoretical analysis and practical applications the subject has become a major area for vigorous growth in the past several years [21-25]. Properties of polymers which have most often been improved include processability, strength, ductility, impact strength, tack/lubricity, abrasion resistance, heat deflection temperature, low-temperature impact/flexibility, flame retardance, permeability, stress-crack resistance, UV resistance, biodegradability, and of course the cost.

### 2.2.2. THEORETICAL MISCIBILITY, PRACTICAL COMPATIBILITY, AND PROPERTIES

For two polymers to be completely miscible, down to the sub-molecular (segmental) level or for a pair of polymer and filler to adhere each other strongly, optimum requirements should be similar polarity,low molecular weights and ease of mixing, in addition to effects like hydrogen bonding or other strong specific intermolecular attractions [20].

Unfortunately most polymer pairs and polymer-filler mixtures do not meet the above requirements for complete or partial miscibility. Their free energies of mixing are positive, and they tend to separate from each other. When the miscibility of pairs is less being irrespective of whether the pairs are polymer-polymer or polymer-filler, then interfacial bonding between them will be weaker. Under stress, these interfaces will fail preferentially and critical properties will not be achieved easily. [26]

Until recently,the above general treatment appeared to explain the results of such systems fairly succesfully. But with the explosion in filler and blend usage in polymer industry during the past few years, however, a great many complications have been accumulating, which indicate the need for much more sophistication, both in basic research and understanding, and also in practical commercialization of the findings. Some of the leading problems may be described as follows:[27]

1) Correlation between polarity and hydrogen bonding on one hand and compatibility of the mixing ingredients on the other, has been far from being succesful,

2) Composition of many commercial polymers is more or less secret, leaving the researcher unable to explain the different behavior of different members of the same polymer family,

3) The interface in most cases is a very minute area, and analytical techniques are rarely capable of describing its structure and function clearly,

4) It is often assumed that the shape of the property vs. ratio curve ( polymer-polymer or polymer-filler or both ) is a measure of the separation of the interface but the relation to molecular weight, moleculer weight distribution, surface area, surface selectivity, domain size in polyblends is not clear,

5) There is some indication that simple low-speed tests like tensile modulus and heat deflection temperature are relatively gross properties, whereas complex dynamic tests are more apt to distinguish fine-scale separations thus the test

method must be choosen both with respect to (a)-Theoretical research objectives and (b)-Relevance of properties to specific practical applications.

The wide range of these observations indicates both the complexity of the problems discussed above and also the broad scope for the accelerating commercial development of filled polymer systems as a major sector of the polymer industries in the years to come.

## 2.3. BASIS OF DYNAMIC MECHANICAL ANALYSIS

### 2.3.1. FUNDAMENTALS

One of the remarkable features of polymers is their sharply expressed viscoelastic properties that give birth to a unique complex of fundamental physical and mechanical properties.

It is general knowledge that the isotropic, homogeneous completely elastic solids when subjected to a small deformation obey Hook`s law [28-31].

$$\sigma = E.\varepsilon \qquad (1)$$

where $\sigma$ = stress

$\varepsilon$ = strain

E = modulus of elasticity.

The behaviour of Newtonian liquids is usually well described by Newton`s law

$$\sigma_{xy} = \eta . \frac{\delta v}{\delta t} \qquad (2)$$

where $\sigma_{xy}$ = shear stress in xy plane

$\eta$ = viscosity

$\frac{\delta v}{\delta t}$ = velocity gradient of liquid.

In actual conditions there are no ideal Newtonian liquids completely deprived of elasticity, as there are no ideally elastic solids that obey Hooke`s law in any conditions of deformation. J.Maxwell was one of the first to pay attention to this fact. All real solids have both elastic and viscous properties to a certain extent. The viscoelastic behaviour of many materials manifests itself only slightly, however, and for this reason they are related to one of the two kinds of solids indicated above.

Polymer materials, usually display properties of both elastic solids and liquids.This leads to a specific relationship between the stress and strain.

### 2.3.2. RELATIONSHIP BETWEEN STRESS AND STRAIN

The relationship between the stress $\sigma$, changing according to a periodic law for viscoelastic bodies, and the strain $\varepsilon$, can be represented as

$$\sigma = E^{*}.\varepsilon \qquad (3)$$

Here $E^{*}$ is the complex modulus of elasticity and equals to

$$E^{*} = E` + i\ E`` \qquad (4)$$

The real part of the modulus of elasticity $Re[E^{*}] = E`$ is called the dynamic modulus of elasticity, and the imaginary part $Im[E^{*}]=E``$ is the loss modulus.

Expression (3) is of great importance for describing the behaviour of polymer materials subjected to the action of periodically changing stresses. Assume that a sinusoidally changing stress is applied on a body; then the stress is given by:

$$\sigma = \sigma_o \sin (\omega\ t)$$

where $\sigma_o$ = amplitude of the stress

$\omega$ = angular frequency ($\omega = 2\pi\nu$, in which $\nu$ is the frequency of the oscillations)

t = time.

In this case, if a body displays linear viscoelastic behaviour, its strain will also change sinusoidally, but will differ in phase from the stress, namely,

$$\varepsilon = \varepsilon_o \sin (\omega t - \delta)$$

where $\varepsilon_o$ = amplitude of the strain

$\delta$ = phase shift between stress and strain.

At any moment of time

$$E^* = \sigma / \varepsilon \qquad (5)$$

A stress that changes according to a sinusoidal law does not coincide in phase with the strain, can be resolved into two components, one of which will coincide in phase with the strain, and the other differ from it in phase by $(\pi/2)$. This makes clear the meaning of the quantities E\` and E\`\`.

### 2.3.3. DYNAMIC MODULUS OF ELASTICITY

By the modulus of elasticity it is meant that the magnitude of the stress that must be applied for the strain (relative deformation) of a material to be equal to unity.

The dynamic modulus of elasticity, E\`, is the real part of the complex modulus. It is equal to the ratio between the component of the stress coinciding in phase with the strain and the value of this strain. The dynamic modulus characterizes the amount of energy received and given up by a unit of volume of a given body during one period.

### 2.3.4. LOSS MODULUS

The loss modulus, E``, is the ratio between the stress component, lagging in phase by ($\pi/2$) from the strain, and the value of the strain. The loss modulus E`` characterizes the part of the energy of elastic oscillations that is transformed into heat during one period of oscillations. When the phase shift between the stress and strain becomes the greatest, E`` passes through a maximum. Thus E`` characterizes the dissipation of the oscillation energy in a viscoelastic body.

The absolute value of the complex modulus of elasticity is:

$$|E^*| = \sqrt{(E')^2 + (E'')^2} \qquad (6)$$

On the other hand, the relationship between the amplitude values of the stress and strain can be written as:

$$\frac{\sigma_o}{\varepsilon_o} = \sqrt{(E')^2 + (E'')^2} \qquad (7)$$

The phase shift between the stress and strain is usually set by the slope of the mechanical losses

$$\tan \delta = \frac{E``}{E`} \qquad (8)$$

which is called the mechanical loss factor or loss tangent.

The relationship between the components of $E^*$ and the phase shift $\delta$ can easily be established from the vector diagram given in Figure 2.

It is clear from the vector algebra that :

$$E` = |E^*| \cos \delta \qquad (9)$$

$$E`` = |E^*| \sin \delta \qquad (10)$$

As a summary, it is strongly pointed out that DMA (Dynamic Mechanical Analysis) is a very useful and important technique because it gives a lot of information to define the viscoelastic characteristics of the polymeric materials.

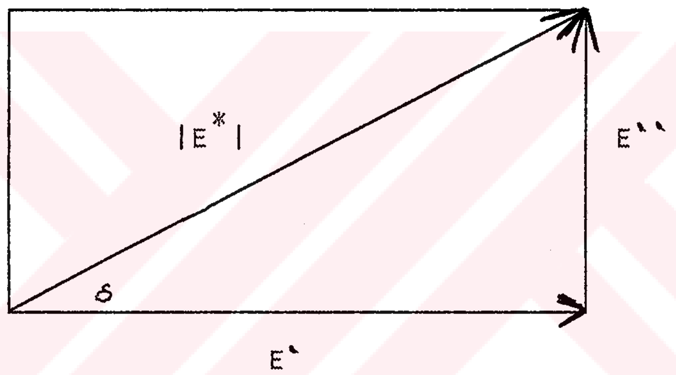


Figure 2. Relationship between components of complex modulus of elasticity $E^*$ and phase shift $\delta$.

# 3. EXPERIMENTAL

## 3.1. MATERIALS

### 3.1.1. SBR 1502

SBR 1502 [32,33] is a cold-continuously polymerized, non-pigmented, non-staining, emulsion type, styrene-butadiene rubber with 23.5 % of bound styrene. Its density is 0.94 gram/cc. It has a weight average molecular weight, $\bar{M}_w$ of 320 000 to 400 000 and a number average molecular weight, $\bar{M}_n$ of 80 000 to 110 000. Heterogeneity indices may range from 3 to 5. It has been obtained from YARPET-PETKIM As. (Petrochemical Industries Corporation of Turkey) directly and has the following chemical and physical properties:

Chemical properties :

| | | Min. | Max. |
|---|---|---|---|
| Volatile matter | wt. % | - | 0.75 |
| Total ash | wt. % | - | 1.50 |
| Organic acid | wt. % | 5.0 | 7.0 |
| Free soap | wt. % | - | 0.5 |
| Bound styrene | wt. % | 21.5 | 25.5 |

Physical Properties :(by suppliers)

| | Min. | Max. |
|---|---|---|
| Raw Polymer Mooney (ML/4` 100 °C) | 45 | 57 |
| Compound Mooney (ML/4` 100 °C) | - | 86 |
| Properties of Vulcanizate (25 °C): | | |
| Tensile Strength (35` cure at 145 °C) | | 225 (MPa) |
| Ultimate Elongation (35` cure at 145 °C) | | 350 % |
| Modulus at 300 % Elongation : | | |
| (25` cure at 145 °C) | 102 | 137 (MPa) |
| (35` cure at 145 °C) | 140 | 175 (MPa) |

### 3.1.2. SBR 1516

BUNA EM SBR 1516 [34] is an emulsion type styrene-butadiene copolymer with 40 % bound styrene in the polymer. It is polymerized with the aid of rosin acid/fatty acid soaps in an aqueous emulsion at + 5°C and contains a non-staining stabilizer. It is a product of BAYER AG-HÜLS AG company and it was obtained directly from the company. Typical data of this rubber is given below:

| | | |
|---|---|---|
| Density | $g/cm^3$ | 0.96 |
| Volatiles | % | max. 0.75 |
| Ash | % | max. 1.0 |
| Bound styrene | % | 40.0 |
| Mooney viscosity ML (1+4) | 100 °C | 40 |

### 3.1.3. SBS KRATON 1101

It was poly(styrene-b-butadiene-b-styrene) rubber and obtained from the Shell Chemical Company [35].It was designated as Kraton 1101, and contained no additives other than an antioxidant. The polymer contains 28 % polystyrene and 72 % polybutadiene. The number-average molecular weight is 13 000 for the styrene blocks. The overall weight-average molecular weight of the block copolymer is 84 000, and the heterogeneity index is 1.21. The polybutadiene chains contain 46 % trans-1,4, 46 % cis-1,4, and 8 % vinyl structures.

### 3.1.4. CARBON BLACK

Carbon black is the Petkara ISAF N-220 [36] (Intermediate Super Abrasion Furnace) grade of PETKIM As. and directly obtained from the company. Its specific gravity is 1.8 and surface area is measured as 114.8 $m^2/g$ by a mercury porosimeter.Its particle size is given as 20-25 nm in the literature [37].

### 3.1.5. BAUXITE

It is a product of ETIBANK-MILAS BAUXITE MINE CORPORATION and directly obtained from the company [38].It is mainly $Al_2O_3$ and contain other oxides in trace amount. It has a melting point of 2000 °C. It is shapless and insoluble in hot and cold water. Its specific area is measured as 6.6 $m^2/g$ by mercury porosimeter and has a specific gravity of 3.66. Its particle size is measured as 1500 nm on average by a sedimentation technique. The data of this analysis are given in the Figures 3-8.

### 3.1.6. SILL CELL 150

Sill-Cell 150 is a light weight filler produced by an Austrian company, STAUSS [39]. It is an inert inorganic filler being composed of spherical, rod-shaped and flaky particles. Three types of Sill-Cell were used during the study namely Sill-Cell 150 (surface untreated), Sill-Cell 150 H (silane treated) and Sill-Cell 150-23 (silicone treated). All these three types of Sill-Cells were obtained from the company directly and they were used as received. The company supplied technical data about Sill-Cell are given below:

<u>Chemical Analysis</u>:

| | |
|---|---|
| $SiO_2$ | 73 % |
| $Al_2O_3$ | 17 % |
| CaO | 1 % |
| $K_2O$ | 5 % |
| Other elements | Traces |
| Loss on ignition | No measurable loss |

| | |
|---|---|
| Moisture | < 0.4 % |
| pH value | 7.0 |

Screen Analysis:

Particle size range (nm) : 5000-150 000

Particle diameter range (nm): 45 000

Typical particle size analysis:

| | |
|---|---|
| > 290 μm | - |
| 150-290 μm | 3 % |
| 74-150 μm | 23 % |
| < 74 μm | 74 % |

Physical Data:

Apparent density (g/cm$^3$) : 0.25

Bulk weight (g/cm$^3$) : 0.135

Melting point (°C) : 1260

Sill-Cell 150-H is silane treated and Sill-Cell 150-23 is silicone treated.

## 3.2. APPARATUS

### 3.2.1. PLASMA SYSTEM

System is composed of a vacuum pump, liquid nitrogen trap, Pyrex glass plasma reactor, Plexiglass sample tray, Mc Leod type pressure manometer, rotavop flow control tap, power supply and control unit, and butadiene containing gas tube or styrene containing Pyrex balloon. Fig.1. (See page 12).

### 3.2.2. ELEMENTAL ANALYZER

The instrument used was Hewlett Packard 185 CHN analyzer. The temperature of the oxidation furnace and reduction furnace were 1060 °C and 490 °C respectively. The column oven temperature was 80 °C and the oven shell temperature was 60 °C while the flow rate of the carrier gas was 100 cc/min. during the analysis.

### 3.2.3. PARTICLE SIZE ANALYZER

Particle size analysis were done by a Shimadzu sedimentation technique based SA-CP3 analyzer.

### 3.2.4. AUTOMATIC BLAIN APPARATUS

A German origin Tonindustrie-Seger automatic blain apparatus was used to determine the surface area of one of the samples [40].

### 3.2.5. MERCURY POROSIMETER

A Micromeritics mercury adsorption porosimeter was used.

### 3.2.6. NITROGEN ADSORPTION POROSIMETER

A Micromeritics Model 2280 nitrogen adsorption surface area analyzer was used during the measurements. Operation temperature of the instrument was between 80-100 °C and the method was based on ASTM D-3037 procedure B.

### 3.2.7. BRABENDER PLASTICORDER

A Brabender Plasti-Corder model PLV 151 processibility tester was used to mix the compounds. Master batches were mixed at 100 °C for 2.5 minutes at a rate of 45 rpm. Final batches were mixed with the same apparatus but at 90 °C and for 2.0 minutes at the same speed of mixer rotor.

### 3.2.8. PLATEN PRESS, MOLDS, AND DIES

ASTM tensile standard 3.5 mm wide dies and 2 mm height steel molds were used during the studies. A PHI platen press was used to vulcanize the samples.

### 3.2.9. ABRASION TESTER

It was a Karl Frank, type 564-c abrasive wheel.Its revolution for one run takes approximately 60 seconds. This machine was used to determine the weight loss of material due to abrasion.

### 3.2.10. TENSILE TESTER

Two type of tensile testers were used during the studies of this thesis. One of them was Instron table type machine and the other was again Instron but model 1185 with a microprocessor controlled digital display unit. The gage length, width, and thickness of the samples were 4, 3, and 0.2 cm respectively. The rate of elongation used was 500 mm/min. Minimum and maximum number of the speciments during the measurements were 4 and 9 respectively.

### 3.2.11. HARDNESS TESTER

The hardness tester used during the measurements was a table type, constant weight, time adjustable, and sound warning Drüfen-Messen-Frank type Shore A durometer.

### 3.2.12. INFRARED SPECTROPHOTOMETER

A Nicolet, model 20 S XB type FT-IR spectrophotometer was used in ATR mode for the analysis of some vulcanizates.

### 3.2.13. DYNAMIC MECHANICAL ANALYZER

A Dupont 9900 full computerized system with a Model 983 Dynamic Mechanical Analyzer was used for Tg determinations. The analysis were hold on 0.2 mm amplitude forced vibration resonant frequency mode.

### 3.2.14. RHEOMETER

A Monsanto rheometer was used. Samples were loaded to the instrument without preheating and experiments were carried out in 15 minutes, ± 1° arc of rotation.

### 3.2.15. ELECTRON MICROSCOPE

A Cambridge Stereoscan S4-10 scanning electron microscope was used during the studies.

## 3.3. EXPERIMENTAL PROCEDURE

As it was mentioned before plasma modifications were done by using a plasma reactor shown in Figure 1. The power applied for pps coatings was 30 watt RF for 30 minutes at room temperature. For ppb coatings 10 watt RF was applied for 26 minutes at room temperature and the pressure of the system was 1-1.5 mm mercury during the polymerizations. Another surface modification method used during the experiments was solvent casting method. For this purpose 0.16 gr of 10 000 gr/mol. molecular weight polystyrene was dissolved in ether and then the desired amount of carbon black was put in the beaker. Ether was evaporated while the mixture is stirred and then the contents of the beaker were dried in a vacuum oven at 50 °C for 24 hours.After surface modification the fillers were loaded to the matrix by using the recipe given on page 41. The master batch was mixed at 100 °C for 2.5 minutes and final batch was mixed at 90 °C for 2 minutes in a Brabender Plasticorder mixer head. Then the compounds were compression molded at 160 °C for 25 minutes for vulcanization. For this purpose an electrically heated platen press was used under a compression pressure of 15 000 phi. The thickness of the obtained vulcanizates were 2 mm in average. The tensile strength and % elongations of these 2 mm thick samples were determined by using two different Instron Tensile tester machines as mentioned in the apparatus part. The reason for this was simply to have more precise measurements by checking the accuracies of the instruments with one another. The width of the samples were 3.5 mm and gage lengths were 4.4 mm in average. The rate of elongations were 500 mm/min. and all measurements were done at 25 °C. All DMA measurements were done by using sample sizes of 16x10.5x2 mm (average), length,width and thickness respectively. Particle size determinations for bauxite were done at room temperature after mixing the samples 10 min.(ulltasonic mode) at 120 rpm/min.

# 4. RESULTS AND DISCUSSION

As a brief summary; two kinds of fillers namely; bauxite, and carbon black, were used in SBR matrix with and without surface treatment. The compounds prepared were vulcanized and the products were tested for their mechanical properties.Some of the experiments will be reexplained for better discussion in the coming pages.

The particle size of the carbon black was known from literature and supplier`s technical sheets. It was in the ranges of 20-25 nm.The unknown bauxite was tested with a sedimentation method under the conditions mentioned before and its particle size was found to be 1500 nm on average.The results of these tests are given in Figures 3-8.

The surface area of these samples was measured with a mercury porosimeter, and a nitrogen adsorption porosimeter. The bauxite sample was also tested with an automatic blain apparatus. As a result the specific surface area of carbon black was found to be 114.9 $m^2/g$. The specific surface area of carbon black is given as 110-140 $m^2/g$ in literature [41,42]. On the other hand the specific surface area of bauxite was determined as 6.6 $m^2/g$.

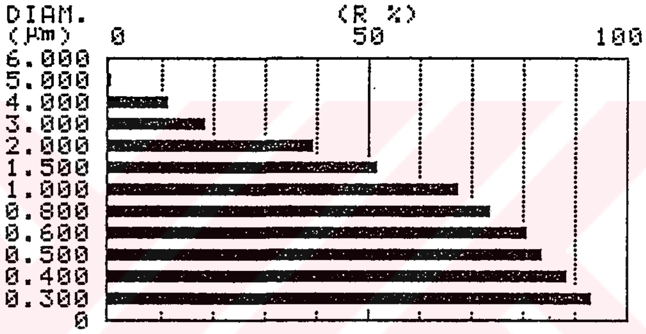
```
<PARTICLE SIZE DISTRIBUTION DATA>

      DIAM.       TIME      ABS.  CHANGE   CUM
      (μm)                         (%)    (R %)

01    6.000    0:00:07    0.906             0
                                   0.6
02    5.000    0:00:10    0.904             0.6
                                  11.1
03    4.000    0:00:15    0.874            11.7
                                   7.3
04    3.000    0:00:24    0.846            19.0
                                  20.6
05    2.000    0:00:42    0.712            39.6
                                  12.7
06    1.500    0:00:59    0.597            52.3
                                  15.6
07    1.000    0:01:33    0.414            67.8
                                   6.2
08    0.800    0:01:57    0.331            74.0
                                   6.9
09    0.600    0:02:33    0.234            81.0
                                   2.9
10    0.500    0:03:01    0.193            83.9
                                   5.1
11    0.400    0:03:39    0.122            89.0
                                   4.7
12    0.300    0:04:38    0.059            93.7
                                   6.3
13    0                   0               100.0
```

```
<SA-CP3 CUMULATIVE GRAPH>

 SAMPLE ID   ALUMINYUMOKSIT
 SAMPLE #    1
```



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 SAMPLE #    1
```

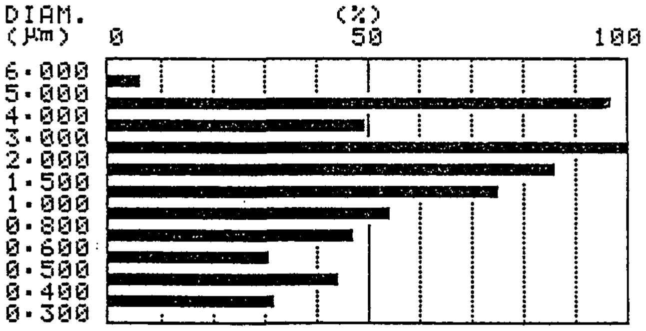

Figure.3. Particle size distribution data of uncoated bauxite.
Sample # 1

```
<PARTICLE SIZE DISTRIBUTION DATA>

      DIAM.      TIME     ABS.  CHANGE   CUM
       (µm)                      (%)    (R %)

01    6.000    0:00:07   0.889            0
02    5.000    0:00:10   0.870    7.8     7.8
03    4.000    0:00:15   0.841   10.0    17.7
04    3.000    0:00:24   0.788   12.8    30.5
05    2.000    0:00:42   0.704   12.3    42.8
06    1.500    0:00:59   0.548   16.0    58.7
07    1.000    0:01:33   0.373   13.9    72.6
08    0.800    0:01:57   0.230   10.0    82.6
09    0.600    0:02:33   0.163    4.5    87.1
10    0.500    0:03:01   0.117    3.0    90.2
11    0.400    0:03:39   0.084    2.2    92.4
12    0                  0        7.6   100.0
```

```
<SA-CP3 CUMULATIVE GRAPH>

 SAMPLE ID  ALUMINYUMOKSIT
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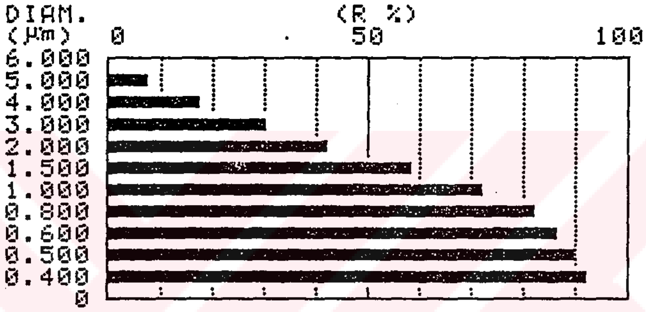


```
<SA-CP3 DIFFERENTIAL GRAPH>

 SAMPLE ID  ALUMINYUMOKSIT
 SAMPLE #   2
```

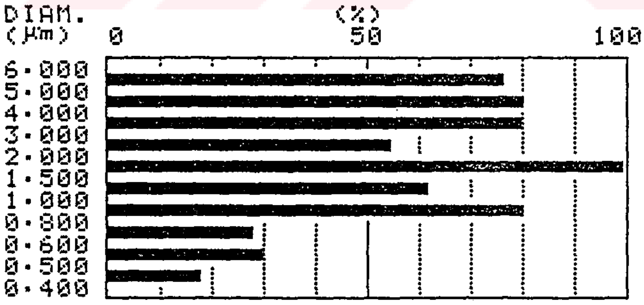


Figure.4. Particle size distribution data of uncoated bauxite. Sample # 2

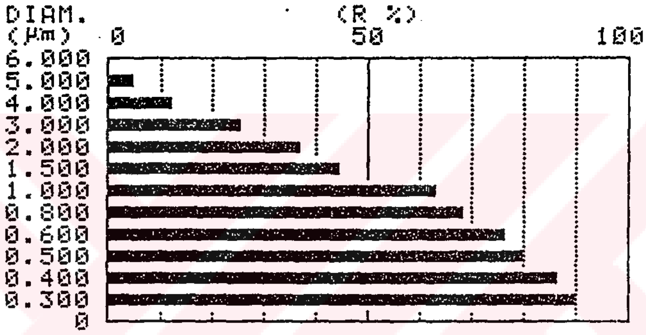
```
<PARTICLE SIZE DISTRIBUTION DATA>

        DIAM.       TIME      ABS. CHANGE  CUM
        (μm)                        (%)   (R %)

01      6.000     0:00:07    0.918           0
02      5.000     0:00:09    0.906   5.2     5.2
03      4.000     0:00:14    0.886   7.3    12.5
04      3.000     0:00:22    0.833  13.5    26.0
05      2.000     0:00:39    0.760  11.2    37.2
06      1.500     0:00:56    0.689   7.6    44.8
07      1.000     0:01:28    0.468  18.7    63.4
08      0.800     0:01:51    0.395   5.3    68.8
09      0.600     0:02:26    0.282   8.0    76.8
10      0.500     0:02:53    0.231   3.5    80.3
11      0.400     0:03:30    0.141   6.4    86.7
12      0.300     0:04:27    0.091   3.7    90.4
13      0                    0       9.6   100.0
```

```
<SA-CP3 CUMULATIVE GRAPH>

 SAMPLE ID   ALUMINYUMOKSIT
 SAMPLE #    3
```



```
<SA-CP3 DIFFERENTIAL GRAPH>

 SAMPLE ID   ALUMINYUMOKSIT
 SAMPLE #    3
```

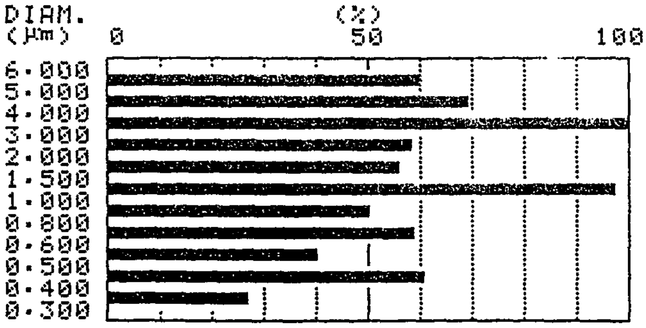


Figure.5. Particle size distribution data of uncoated bauxite. Sample # 3

```
<PARTICLE SIZE DISTRIBUTION DATA>

       DIAM.       TIME     ABS.  CHANGE   CUM
       (µm)                        (%)   (R %)

01     6.000     0:00:07   0.910            0
02     5.000     0:00:09   0.901    4.2     4.2
03     4.000     0:00:14   0.876    8.6    12.7
04     3.000     0:00:22   0.833   10.7    23.5
05     2.000     0:00:39   0.693   20.9    44.4
06     1.500     0:00:56   0.650    4.5    48.9
07     1.000     0:01:28   0.390   21.4    70.3
08     0.800     0:01:51   0.385    0.3    70.6
09     0.600     0:02:26   0.227   11.0    81.6
10     0.500     0:02:53   0.218    0.6    82.2
11     0.400     0:03:30   0.128    6.3    88.4
12     0.300     0:04:27   0.075    3.8    92.3
13     0                   0        7.7   100.0
```

```
<SA-CP3 CUMULATIVE GRAPH>

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 SAMPLE #    4
```
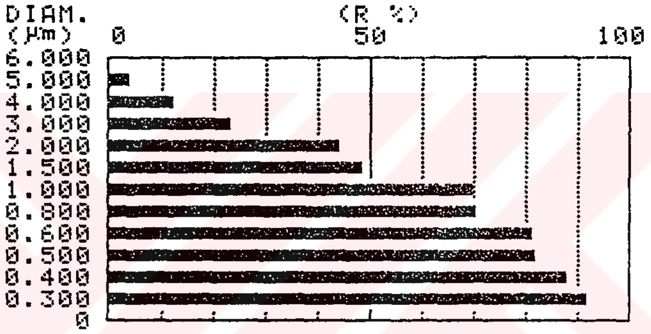



```
<SA-CP3 DIFFERENTIAL GRAPH>

 SAMPLE ID   ALUMINYUMOKSIT
 SAMPLE #    4
```

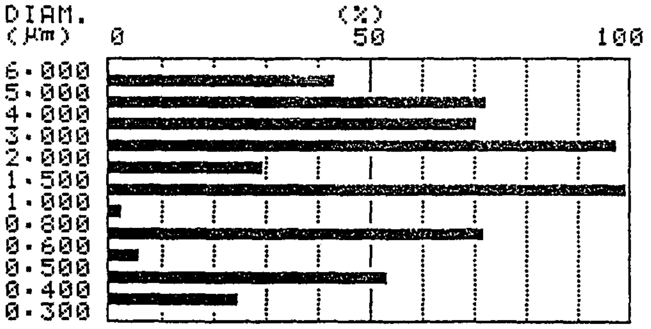
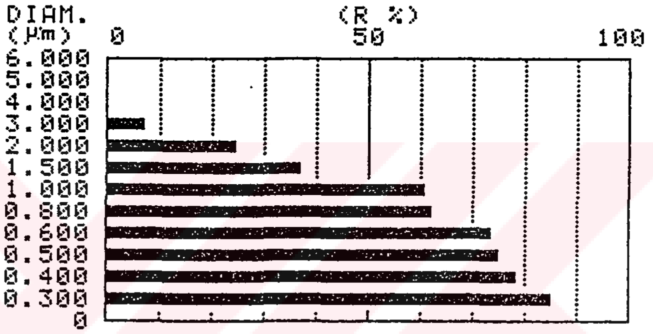


Figure.6. Particle size distribution data of uncoated bauxite. Sample # 4

```
<PARTICLE SIZE DISTRIBUTION DATA>

        DIAM.       TIME      ABS.  CHANGE   CUM
        (μm)                          (%)   (R %)

01    6.000    0:00:07   0.950              0
02    5.000    0:00:09   0.950       0      0
03    4.000    0:00:14   0.950       0      0
04    3.000    0:00:22   0.923     7.2      7.2
05    2.000    0:00:39   0.815    17.8     24.9
06    1.500    0:00:56   0.705    12.6     37.6
07    1.000    0:01:28   0.441    23.8     61.4
08    0.800    0:01:51   0.427     1.1     62.5
09    0.600    0:02:26   0.275    11.5     74.0
10    0.500    0:02:53   0.258     1.3     75.3
11    0.400    0:03:30   0.214     3.4     78.7
12    0.300    0:04:27   0.129     6.7     85.4
13    0                  0        14.6    100.0
```

<SA-CP3 CUMULATIVE GRAPH>

SAMPLE ID   ALUMINYUMOKSIT
SAMPLE #    5



<SA-CP3 DIFFERENTIAL GRAPH>

SAMPLE ID   ALUMINYUMOKSIT
SAMPLE #    5

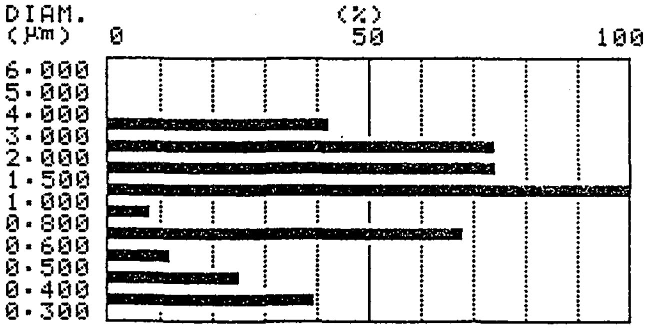
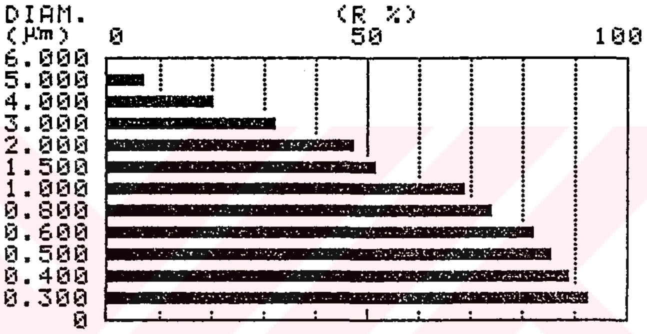


Figure.7. Particle size distribution data of uncoated bauxite. Sample # 5

```
<PARTICLE SIZE DISTRIBUTION DATA>

       DIAM.        TIME      ABS.  CHANGE   CUM
       (µm)                          (%)    (R %)

01    6.000     0:00:07   0.912            0
                                     7.3
02    5.000     0:00:10   0.894              7.3
                                    13.4
03    4.000     0:00:15   0.854             20.7
                                    11.9
04    3.000     0:00:24   0.803             32.6
                                    15.3
05    2.000     0:00:42   0.695             47.9
                                     4.5
06    1.500     0:00:59   0.649             52.4
                                    16.8
07    1.000     0:01:33   0.433             69.2
                                     5.1
08    0.800     0:01:57   0.357             74.3
                                     8.2
09    0.600     0:02:33   0.231             82.5
                                     3.2
10    0.500     0:03:01   0.181             85.7
                                     3.8
11    0.400     0:03:39   0.123             89.5
                                     3.5
12    0.300     0:04:38   0.072             93.0
                                     7.0
13    0                   0                100.0
```

```
<SA-CP3 CUMULATIVE GRAPH>

 SAMPLE ID   ALUMINYUMOKSIT
 SAMPLE #    6
```



```
<SA-CP3 DIFFERENTIAL GRAPH>

 SAMPLE ID   ALUMINYUMOKSIT
 SAMPLE #    6
```

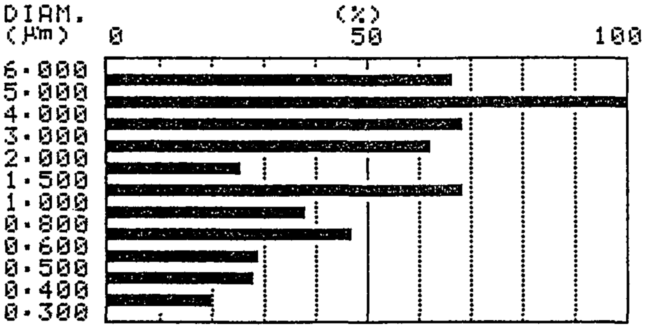


Figure.8. Particle size distribution data of uncoated bauxite. Sample # 6

These two fillers, carbon black and bauxite were used in SBR matrix with the following recipe.

| | | | |
|---|---|---|---|
| SBR | 100 | MASTER BATCH | FINAL BATCH |
| Filler | 35 | | |
| ZnO | 3 | | |
| Stearic acid | 2 | | |
| Antioxidant | 2 | | |
| Sulfur | 2 | | |
| Accelerator | 1.3 | | |

BATCH SIZE = 45.0 gram.

(based on phr)

The ingredients of the above recipe were mixed as a master batch first, and then curatives were added to the system. The compounds prepared by this way were compression molded and vulcanized at the conditions mentioned in the experimental part. Two of these vulcanizates namely one prepared with uncoated carbon black and the other with ppb coated were analyzed with ATR-FTIR spectroscopy separately to trace out chemical differences between the surfaces. Since it was very difficult to see the differences on the surface of fillers by using vulcanizates as samples which brings to the system much complexity no difference was observed in the IR spectra as shown in Figures 9-10.

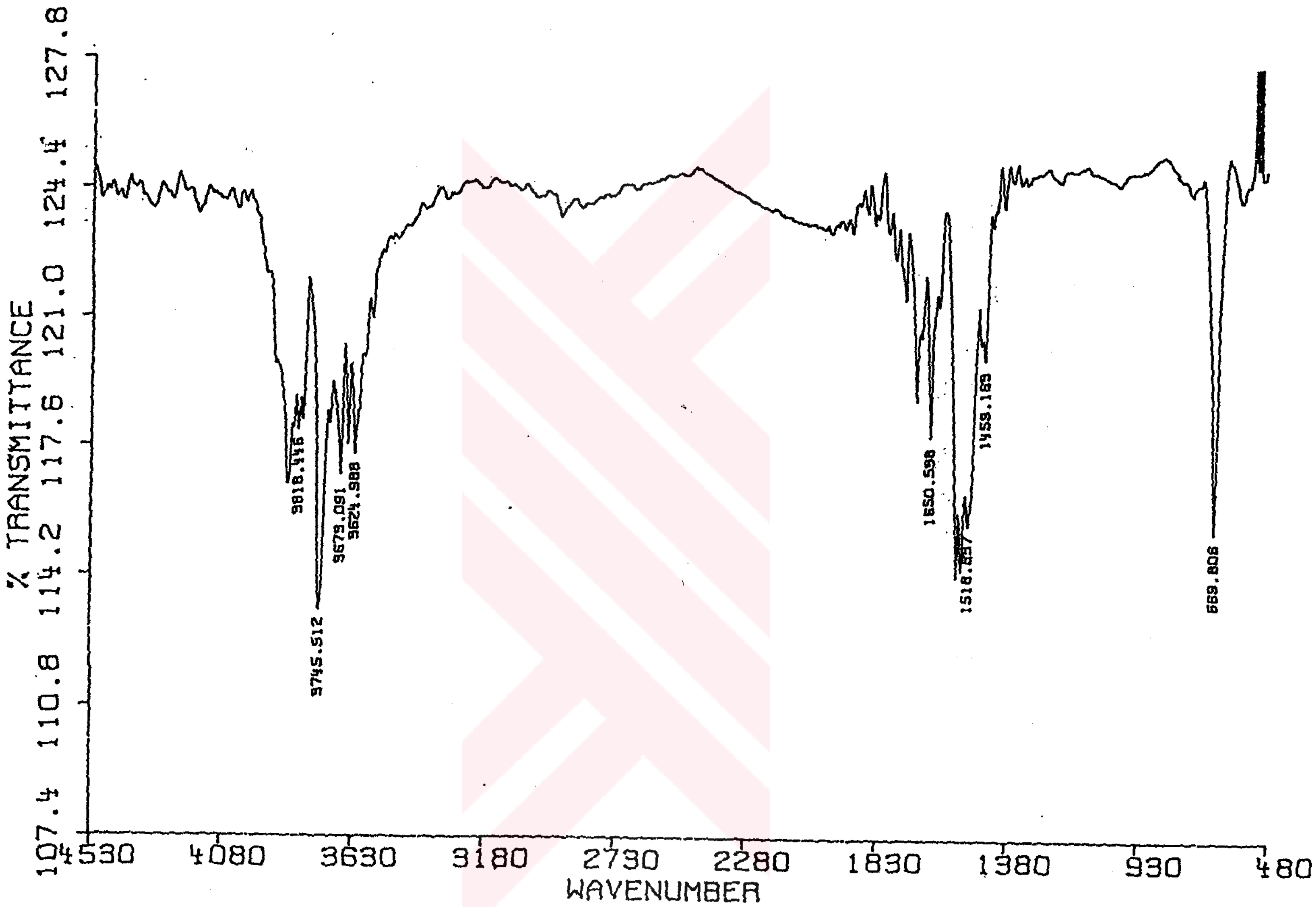


Figure.9. ATR/FT-IR spectra of uncoated carbon black filled SBR 1502 vulcanizate.

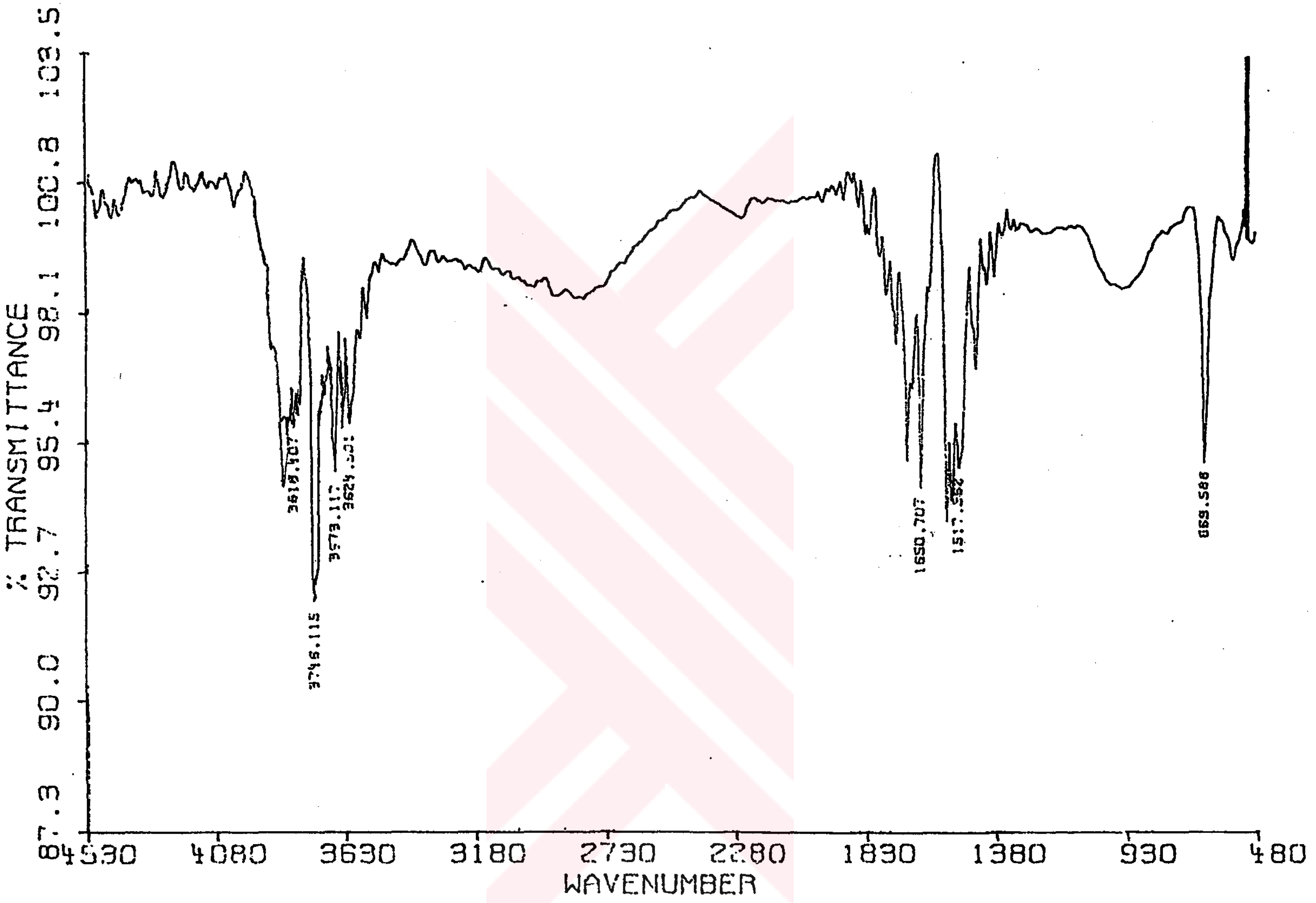


Figure.10. ATR/FT-IR spectra of PB coated carbon black filled SBR 1502 vulcanizate.

Then the vulcanizates were tested for their Tg`s, and basic mechanical properties as hardness, tensile strength and elongation percentages.The results of these tests were summarized Table 1.

As it can be seen from the Table 1. carbon black is 60 or 75 times smaller in particle size while it has approximately 20 times larger surface area than bauxite. In addition to this fact it is well known that carbon blacks are highly porous structures. For this reason when the reinforcing effects of these two fillers was compared it can easily be imagined that carbon black will be more effective than bauxite and that is the finding as shown in Table 1.

In the second phase of the study plasma polymerized polystyrene (pps) and plasma polymerized polybutadiene (ppb) were coated on bauxite and carbon black with plasma polymerization technique. For this purpose a cylindirical Pyrex glass reactor of 40 cm length and 8 cm diameter was used with outer electrodes as shown in Figure 1. For polystyrene coatings 38 watt of rf power was applied for 30 minutes.Polybutadiene coatings were realized by application of 10 watt for 26 minutes. Frequency was 13.56 MHz during both of the coatings while pressure of the system was changing between 1-1.5 mm of mercury.

| SAMPLE | PARTICLE SIZE nm | SURFACE AREA M**2/gm | HARDNESS SHORE A | ABRASION WEIGHT % LOSS | Tg C | Tan d | TENSILE STRENGTH MPa | ELONGATION AT BREAK % |
|---|---|---|---|---|---|---|---|---|
| BAUXITE | 1500 | 6.6 | 50.5 | 19.2 | - 27.0 | 1.6 | 2.85∓0.12 | 240∓50 |
| CARBON BLACK | 20-25 | 114.9 | 66.0 | 7.8 | - 20.0 | 0.9 | 25.98∓3.91 | 639∓56 |

Table.1. Preliminary results of Bauxite and Carbon Black filled SBR 1502 vulcanizates

It was known from ESCA analysis of the surface of carbon particles for such coatings obtained in plasma that the homogeneity of the coat for the samples from the top or from the bottom of the sampling tray are the same [43].

After surface treatment to check the coating ,the coated samples were analyzed with mercury porosimeter and nitrogen adsorption porosimeter. At the end of these analysis it was seen that, specific surface area of pps coated bauxite and carbon black were 6.3 $m^2/g$ and 115.0 $m^2/g$ respectively. So it was concluded that there is no appreciable amount of change in surface area due to the pps coatings. Samples coated with ppb were also analyzed with same technique and it was seen that specific surface area of ppb coated bauxite and carbon black were 3.9 $m^2/g$ and 106.2 $m^2/g$, respectively. It is clear from these results that ppb coatings are more effective under these conditions. This may simply be due to the difference of kinetics of polymerization of styrene and butadiene in plasma.

All pps and ppb coated bauxite and carbon black samples were then used as filler in the recipe given before. The products were processed in the same manner with the previous ones and the vulcanizates were analyzed for the same properties at the end. The results of these tests are given in Figures 11-21, Tables 2-7 and they are all together summarized in Table 8.

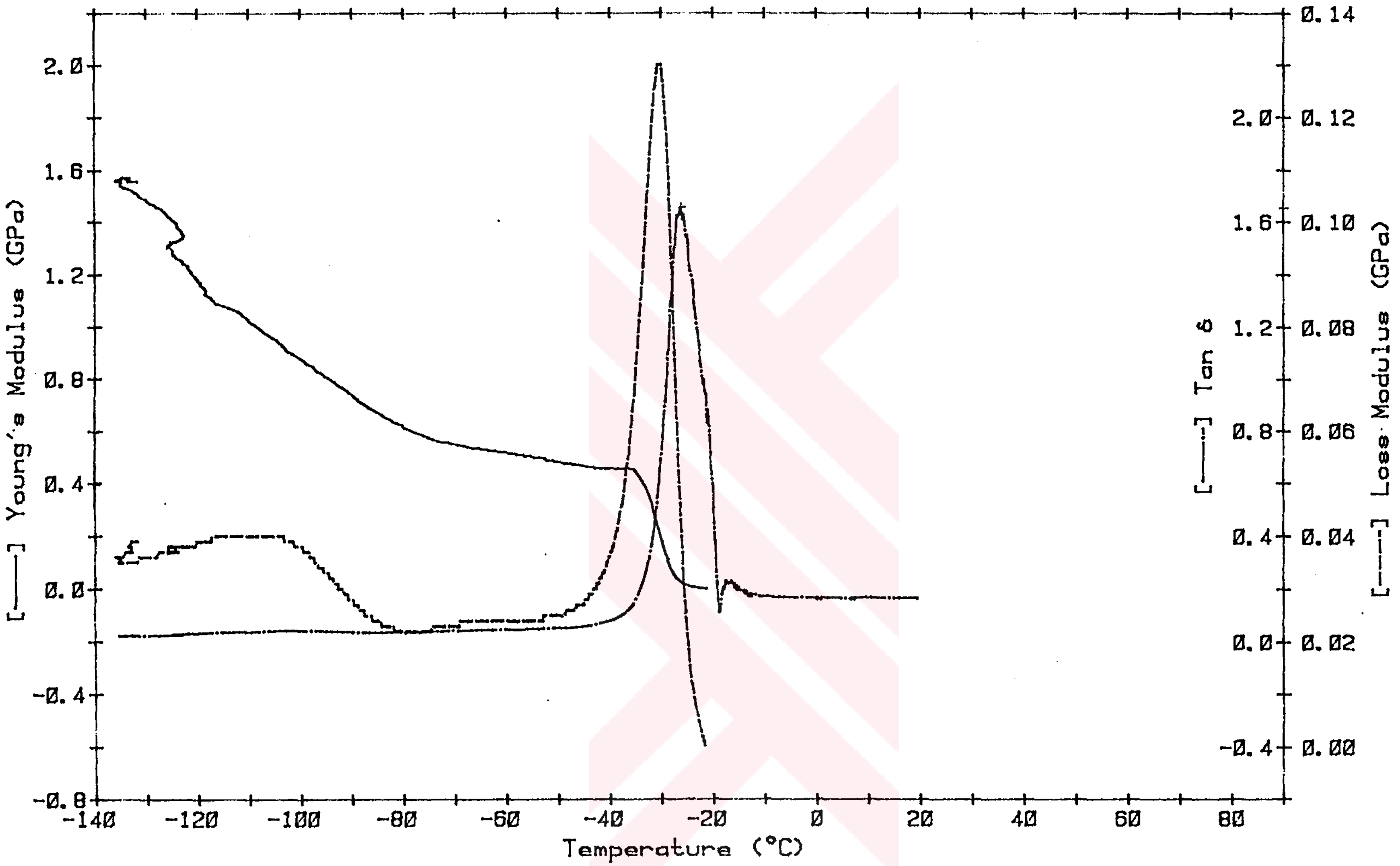


Figure.11. DMA of uncoated bauxite filled SBR 1502 vulcanizate

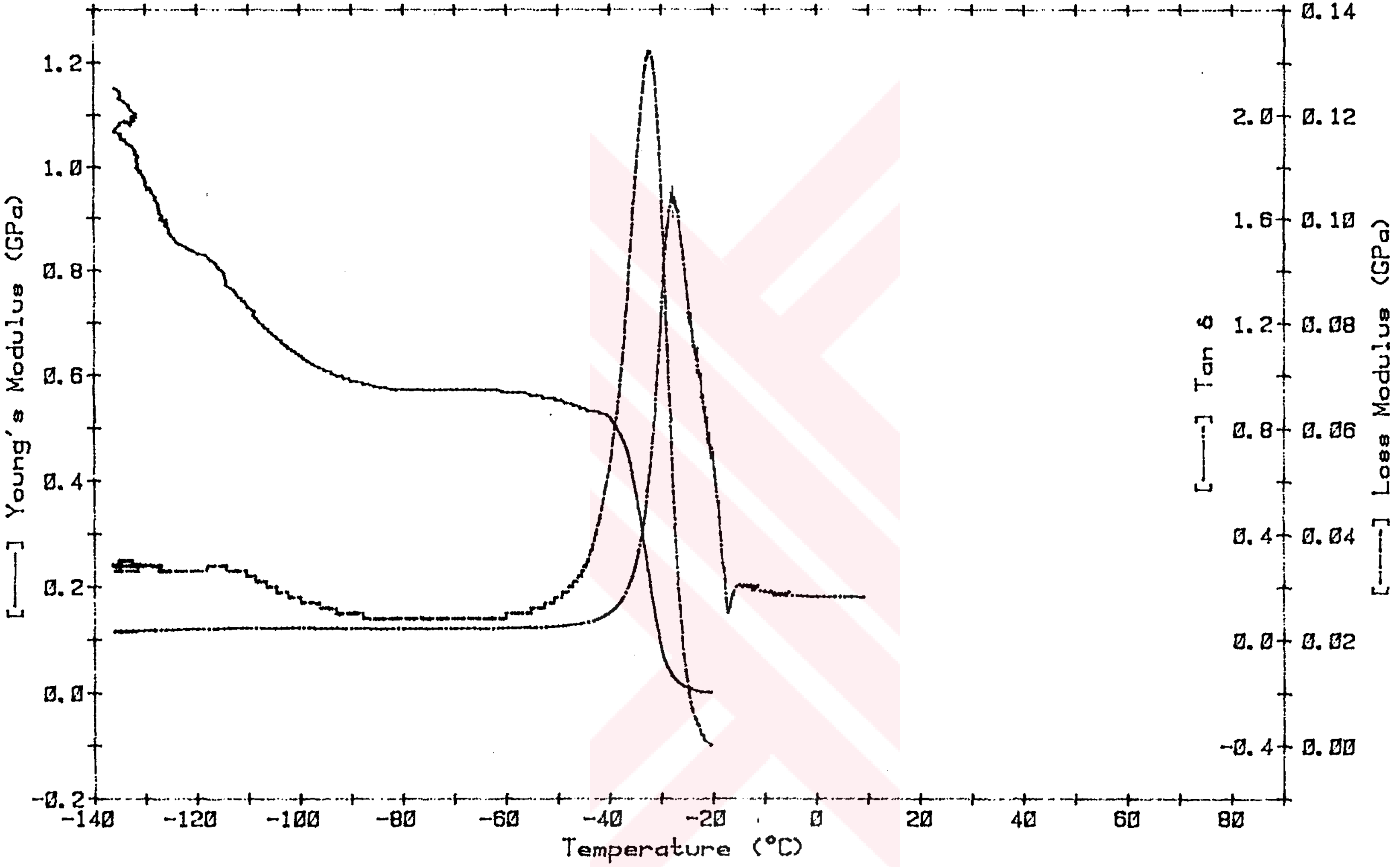


Figure.12. DMA of PPS coated bauxite filled SBR 1502 vulcanizate

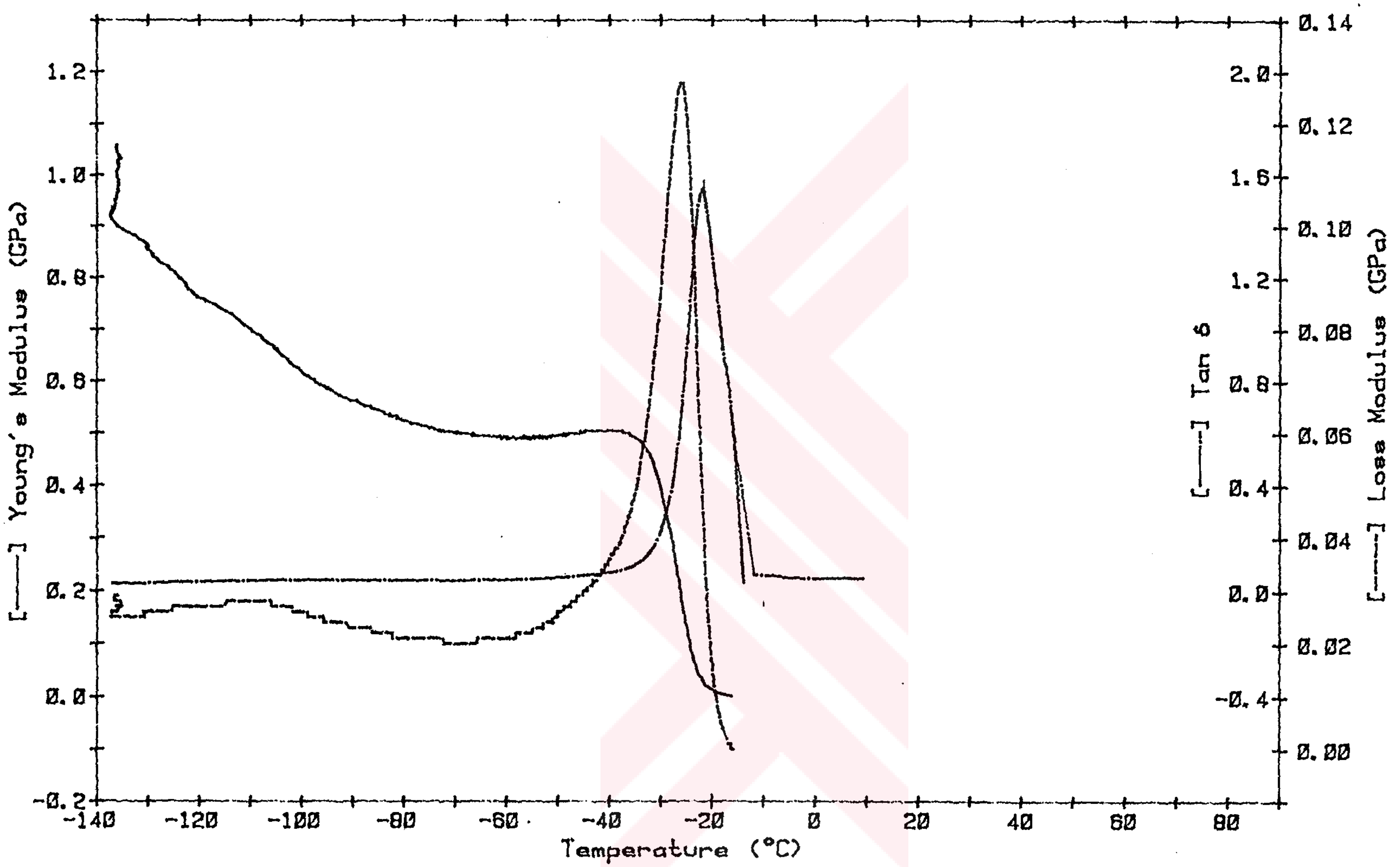


Figure.13. DMA of PPB coated bauxite filled SBR 1502 vulcanizate

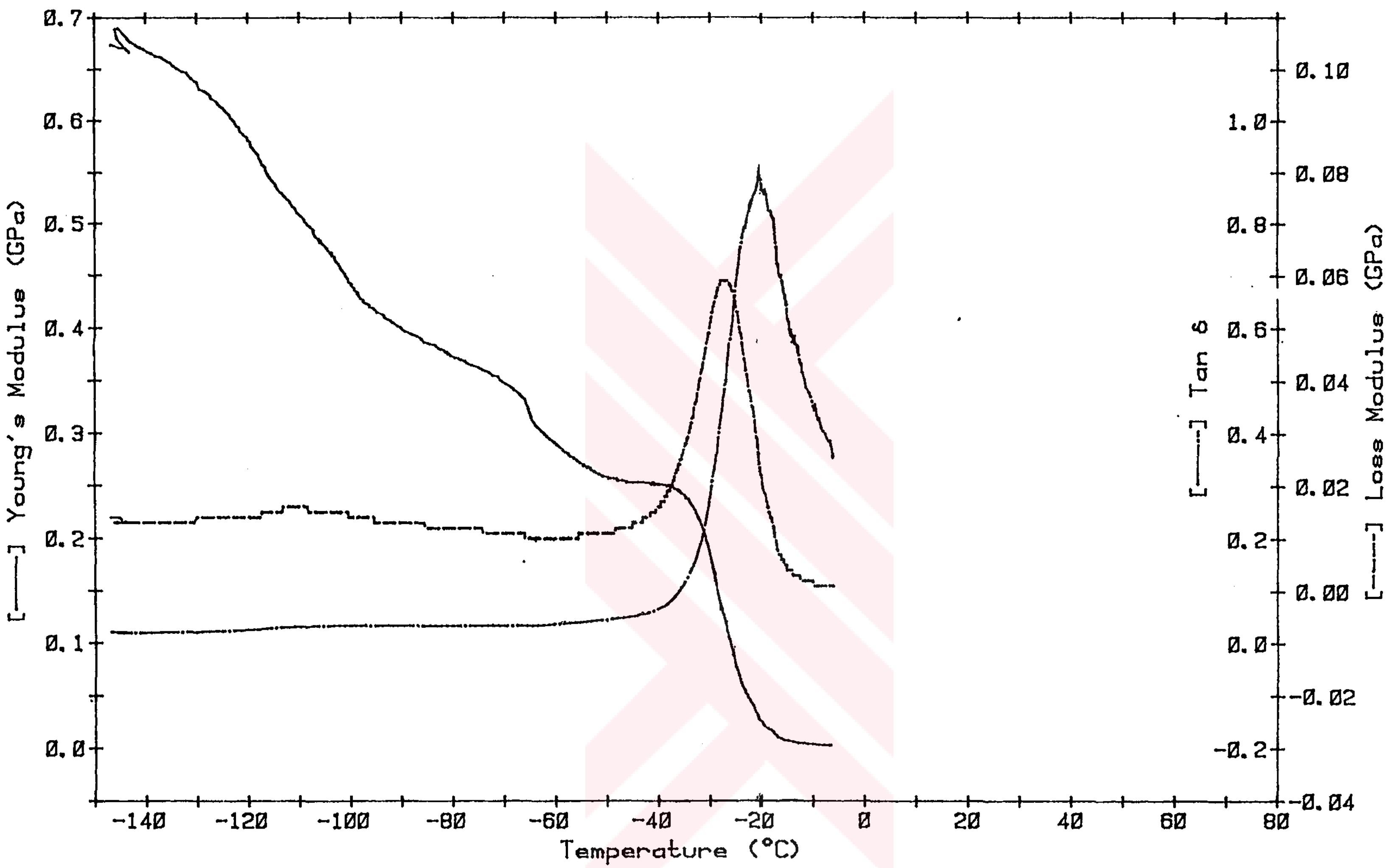


Figure.14. DMA of uncoated carbon black filled SBR 1502 vulcanizate

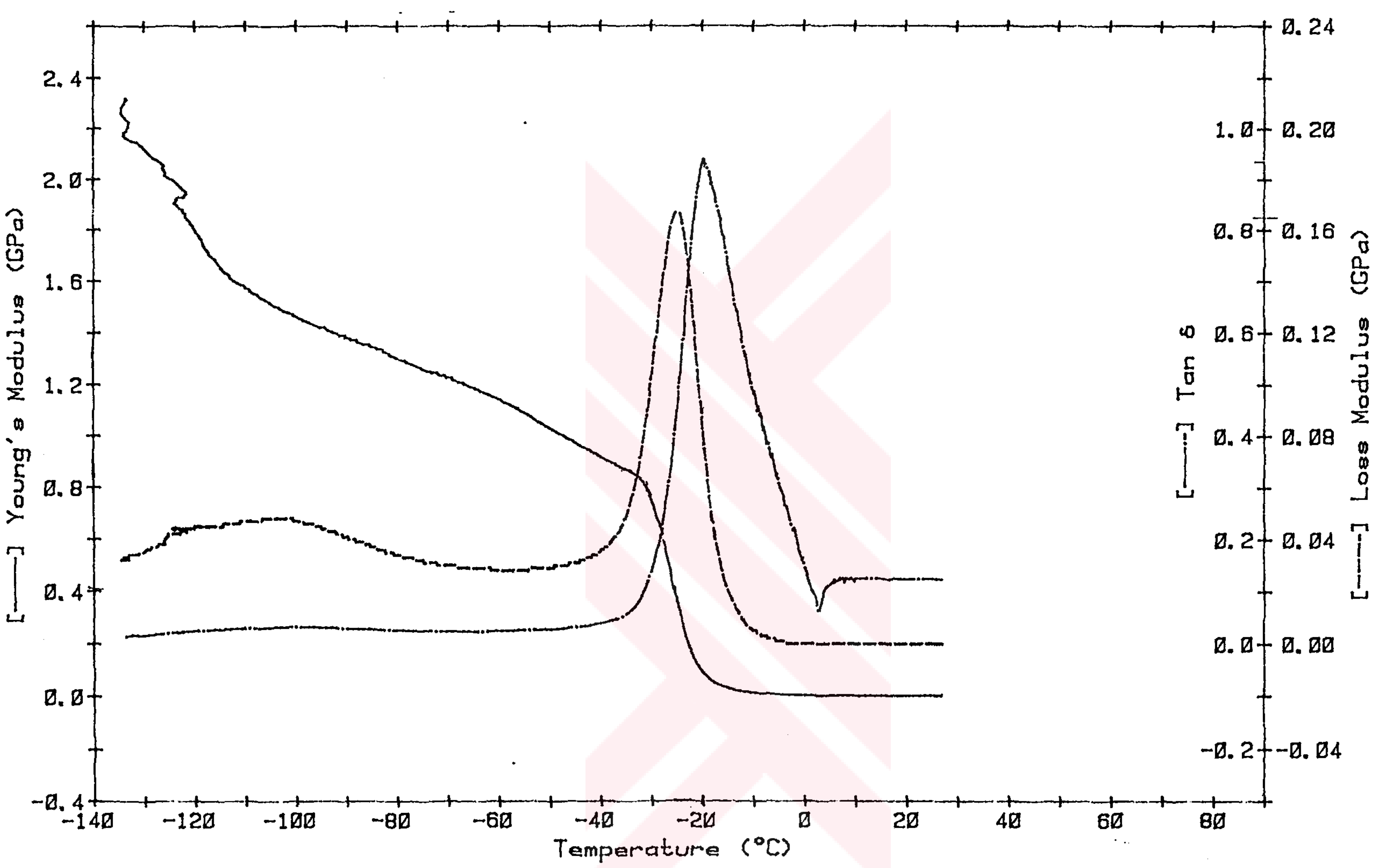


Figure.15. DMA of PPS coated carbon black filled SBR 1502 vulcanizate

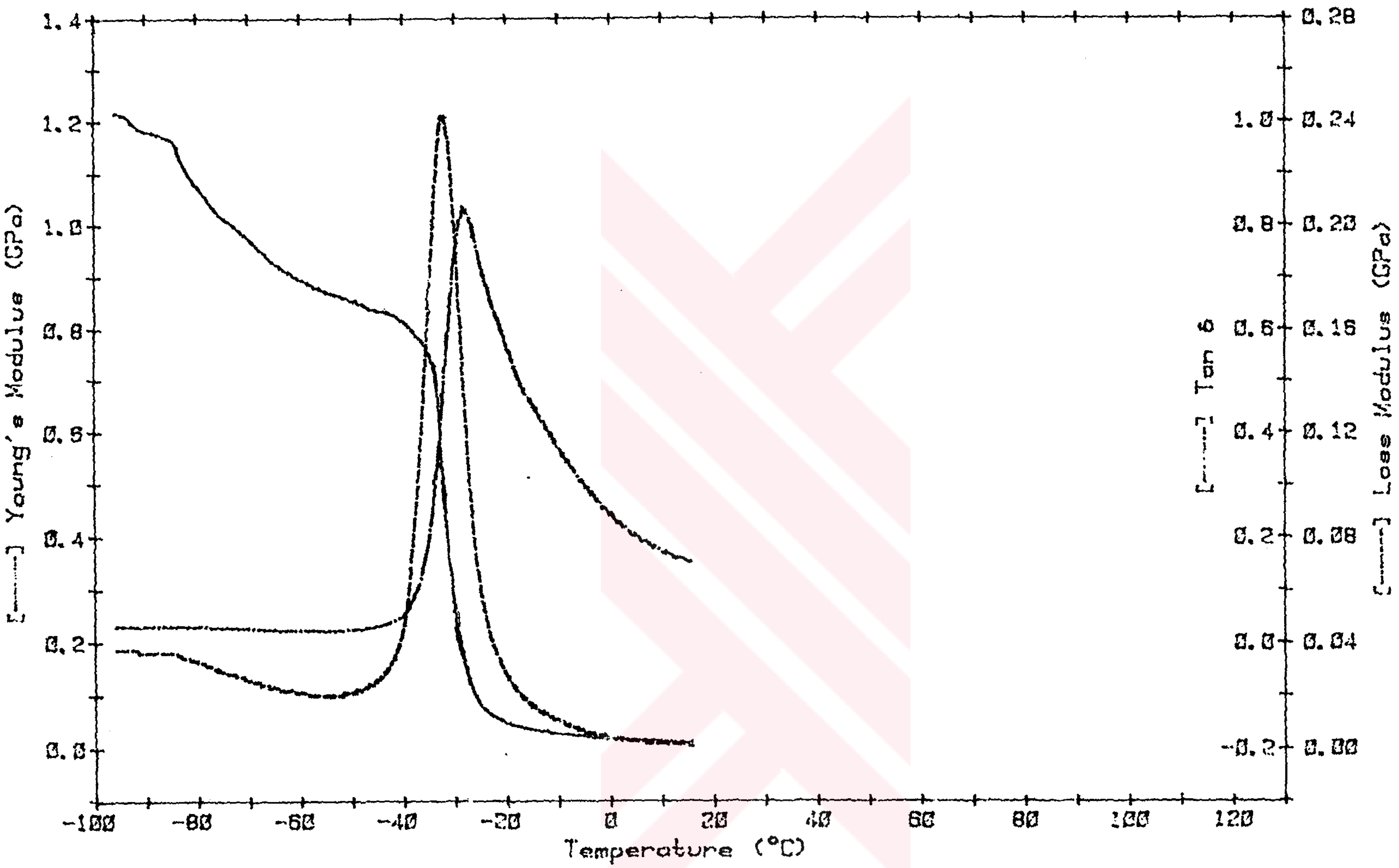


Figure.16. DMA of PPB coated carbon black filled SBR 1502 vulcanizate

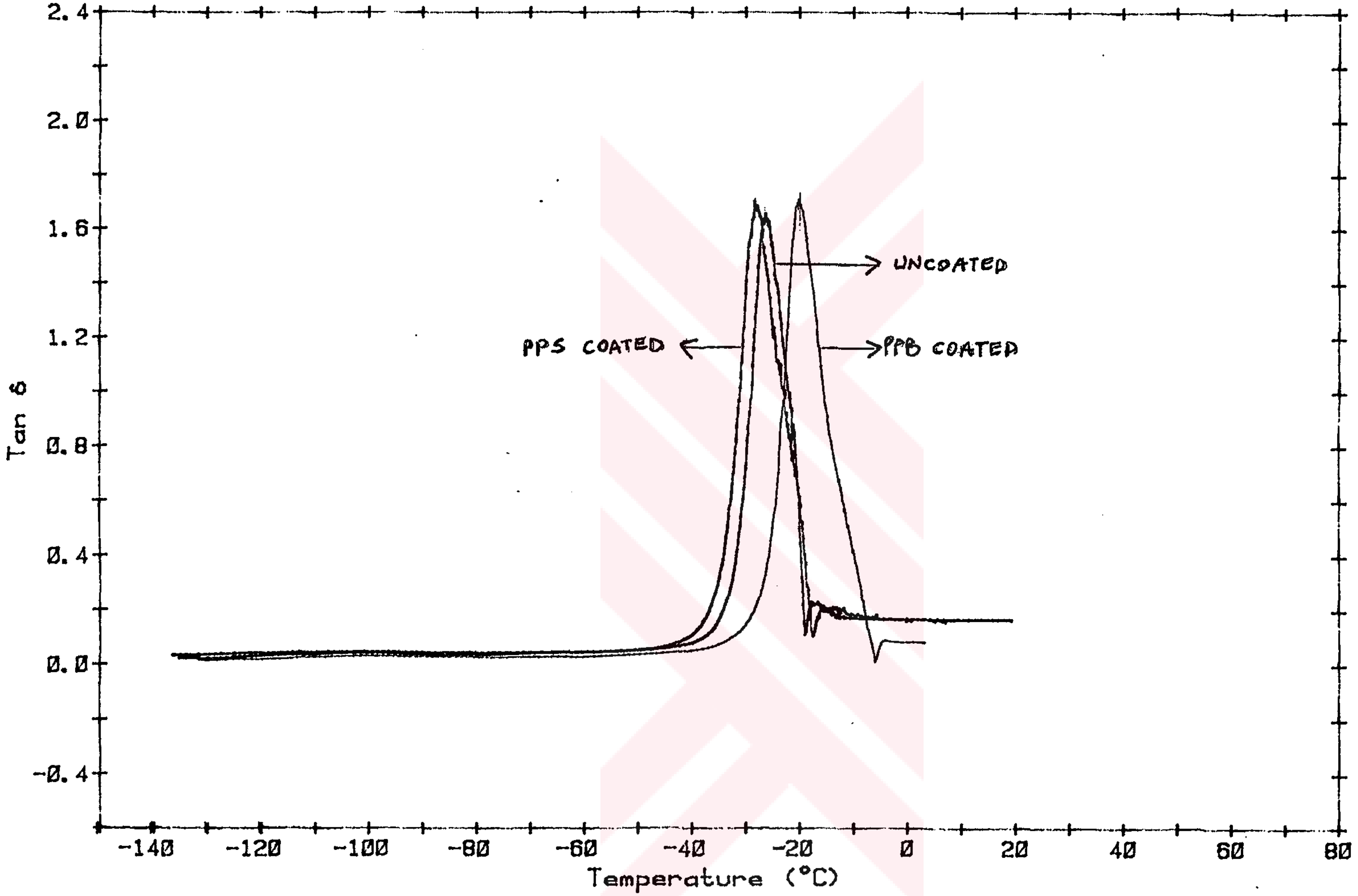


Figure.17. Comparison of Tg values of uncoated, PPS and PPB coated bauxite filled SBR 1502 vulcanizates.

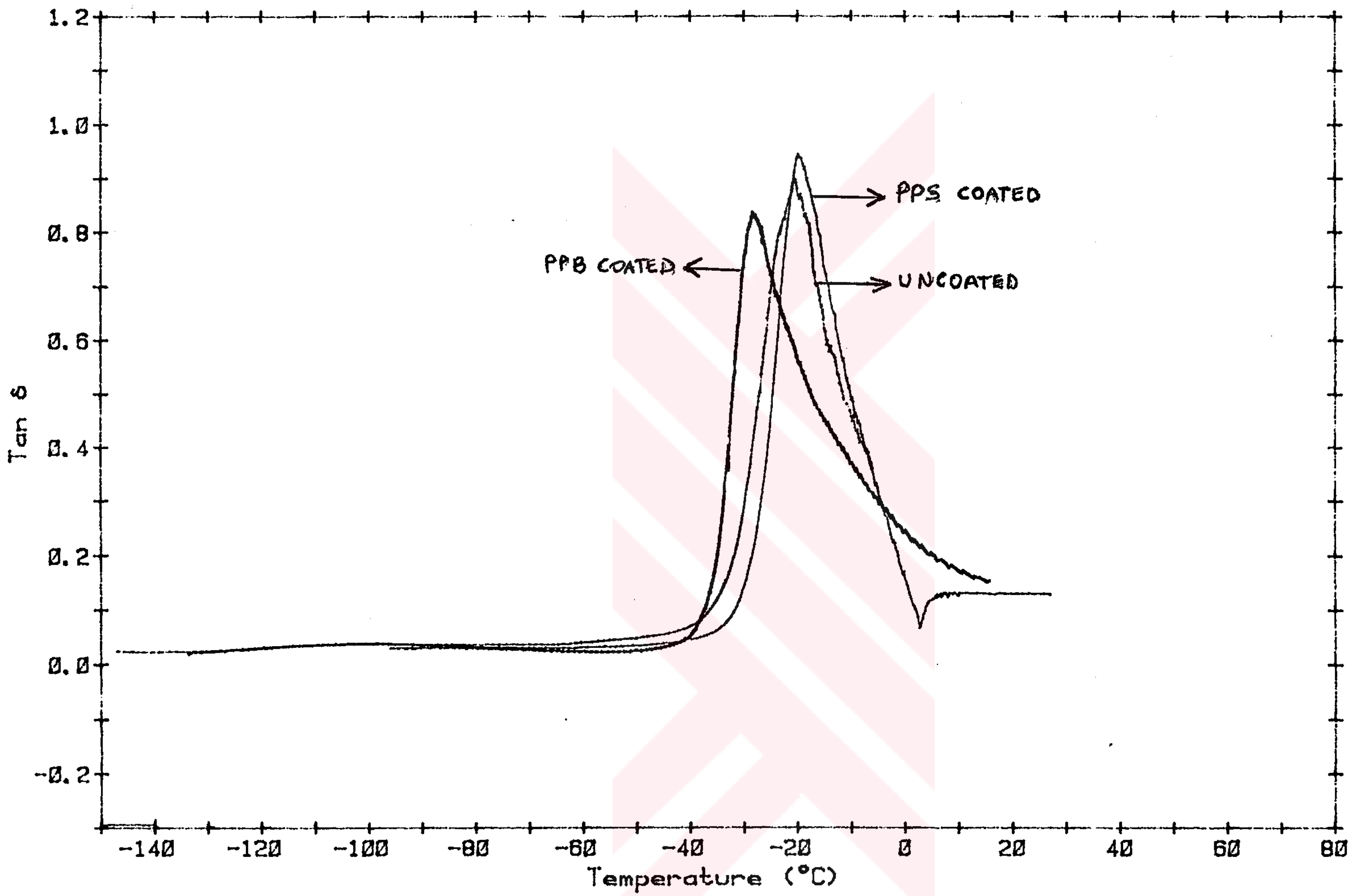


Figure.18. Comparison of Tg values of uncoated, PPS and PPB coated carbon black filled SBR 1502 vulcanizates.

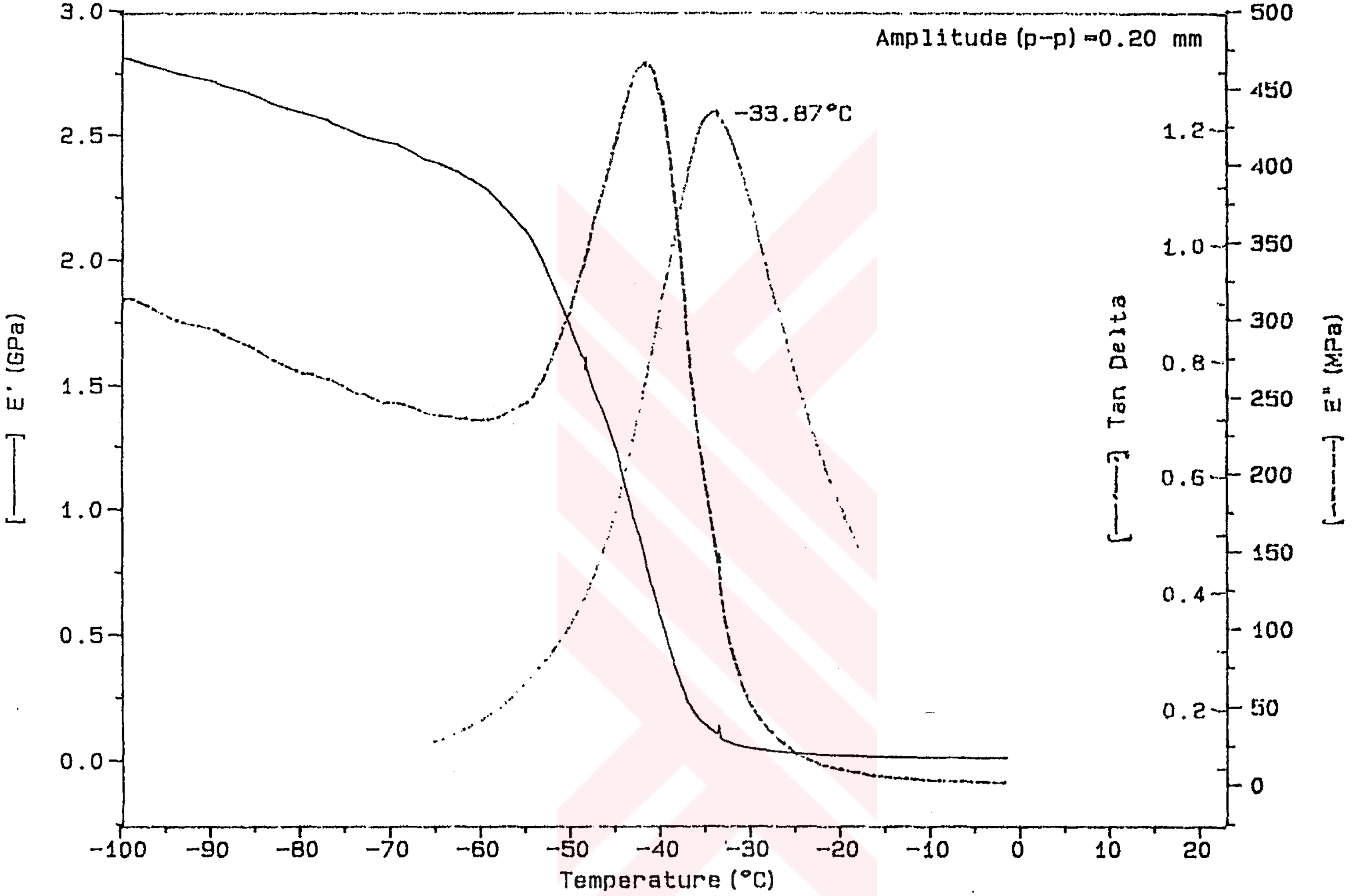


Figure.19. DMA of unfilled SBR 1502 vulcanizate

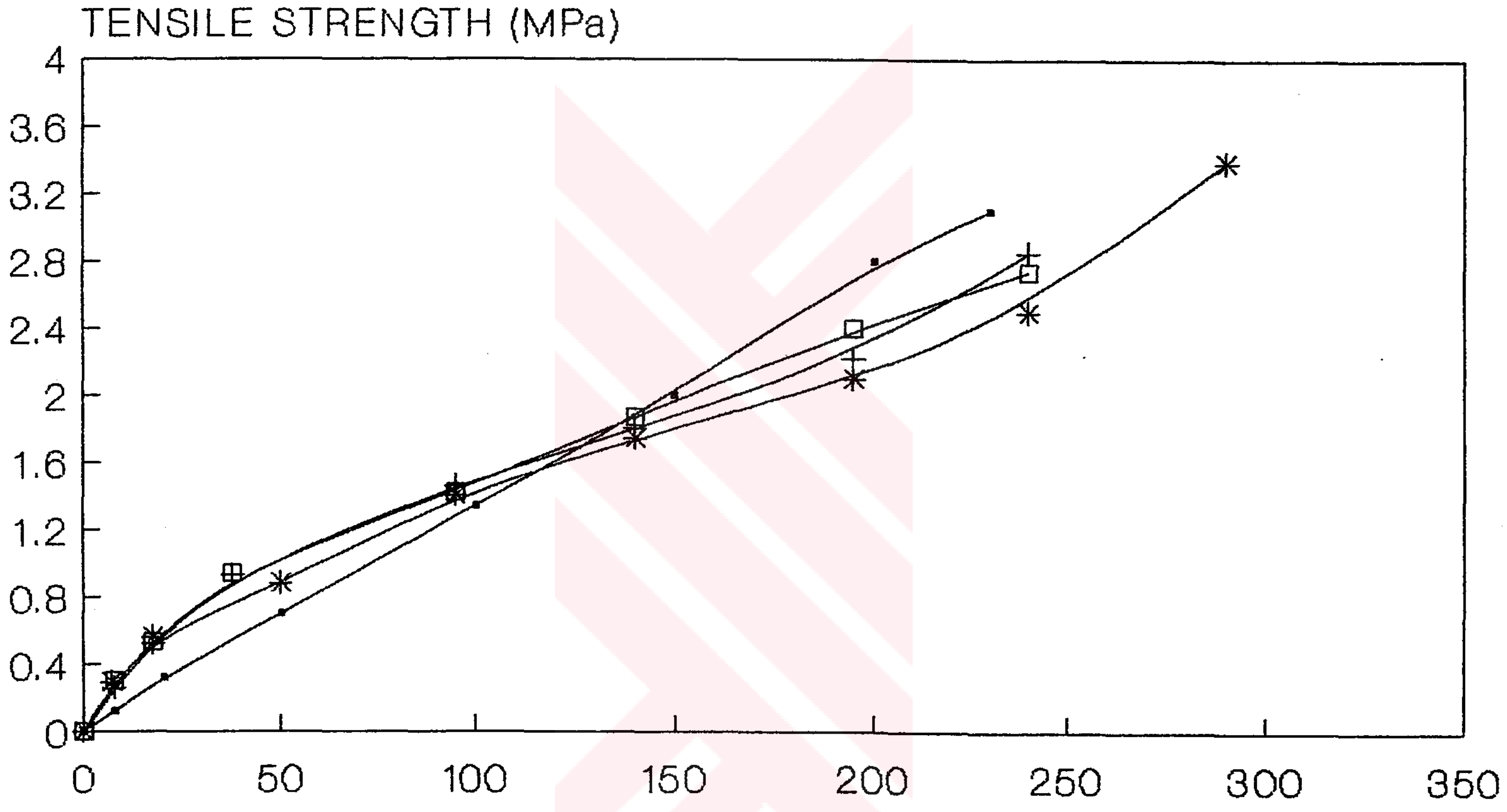


Figure 20. Stress strain curves of unfilled, ● ; uncoated bauxite filled, + ; PPS coated bauxite filled, ✱ ; PPB coated bauxite filled, □ ; SBR 1502 vulcanizates.

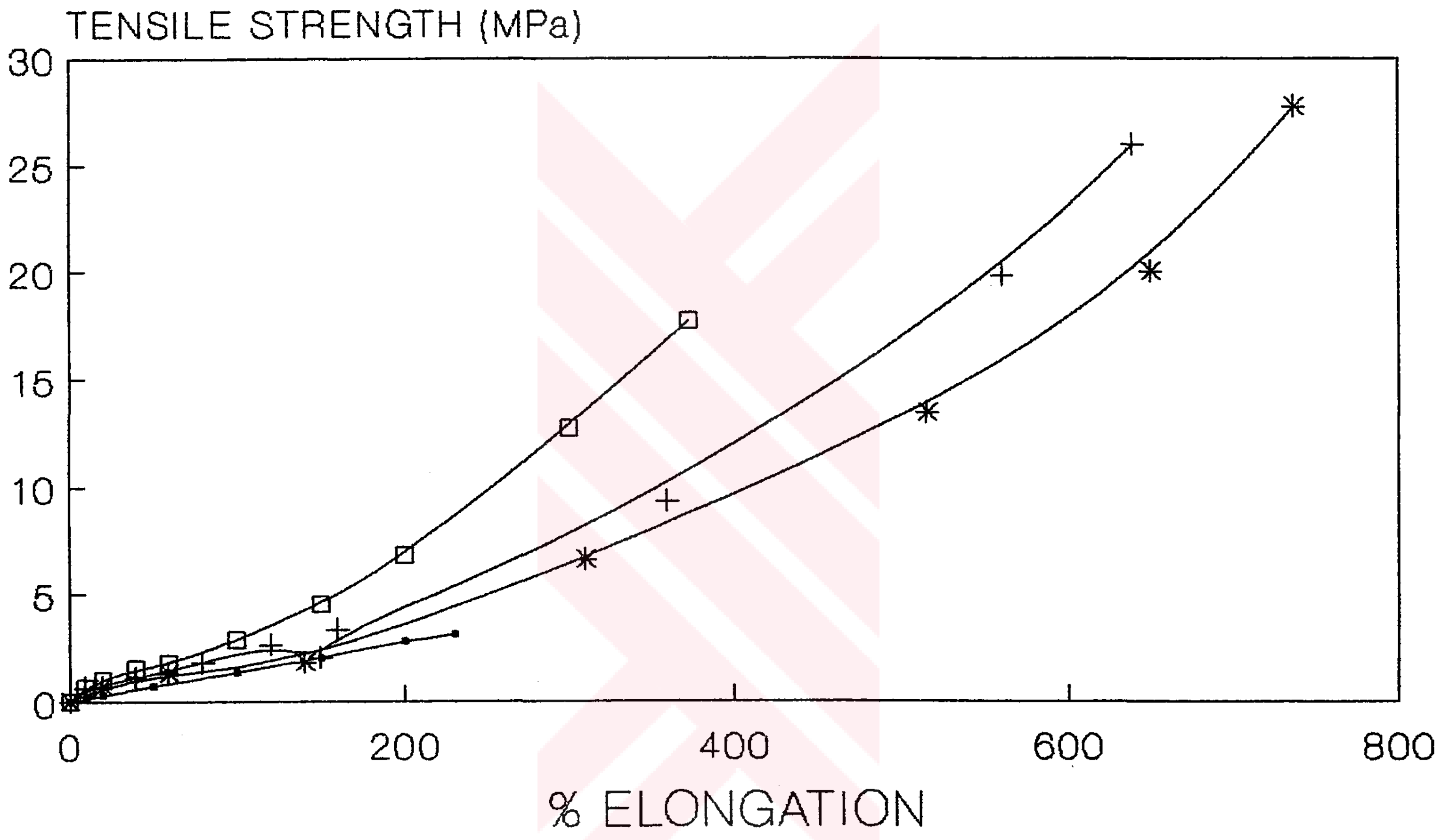


Figure 21. Stress strain curves of unfilled, ● ; uncoated carbon black filled, +; PPS coated carbon black filled, ✱ ;PPB coated carbon black filled, □; SBR 1502 vulcanizates.

```
UNCOATED BAUXITE    SAMPLE WT==0.33gm

PRESSURE  INTRUSION    CUM.      CUM.PORE    SYSTEM
                     INTRUSION    VOLUME    CONSTANT
====================================================================================================================================

       4     31.76          0            0   0.01073

     7.1      31.3       0.46    0.0049358   0.01073                                                            SPECIFIC

    10.5     30.91       0.85    0.0091205   0.01073          AVE.                                   TOTAL      SURFACE =TOTALP*DELTA V*(

    13.2     30.71       1.05    0.0112665   0.01073        PRESSURE     DELTA V    P*DELTA V    P*DELTA V       AREA

====================================================================================================================================

    13.2     34.22       1.05    0.0112665   0.01073          56.6       0.000107   0.006073     97.15281    6.624055
     100     34.21       1.06    0.0113738   0.01073           150       0.012446    1.86702
     200     33.05       2.22    0.0238206   0.01073           250        0.02146      5.365
     300     31.05       4.22    0.0452806   0.01073           350       0.017060   5.971245
     400     29.46       5.81    0.0623413   0.01073           425       0.007296    3.10097
     450     28.78       6.49    0.0696377   0.01073           475       0.007832   3.720627
     500     28.05       7.22    0.0774706   0.01073           750       0.003004     2.2533
    1000     27.77        7.5     0.080475   0.01073          1500       0.003970    5.95515
    2000      27.4       7.87    0.0844451   0.01073          2500       0.000858      2.146
    3000     27.32       7.95    0.0853035   0.01073          4000       0.000858     3.4336
    5000     27.24       8.03    0.0861619   0.01073          6250       0.000751   4.694375
    7500     27.17        8.1     0.086913   0.01073          8750       0.000643    5.63325
   10000     27.11       8.16    0.0875568   0.01073         10500       0.000214     2.2533
   11000     27.09       8.18    0.0877714   0.01073         11500       0.000321    3.70185
   12000     27.06       8.21    0.0880933   0.01073         12500       0.000214     2.6825
   13000     27.04       8.23    0.0883079   0.01073         14000       0.000321     4.5066
   15000     27.01       8.26    0.0886298   0.01073         16250       0.000429     6.9745
   17500     26.97        8.3     0.089059   0.01073         18750       0.000429     8.0475
   20000     26.93       8.34    0.0894882   0.01073         20500       0.000214     4.3993
   21000     26.91       8.36    0.0897028   0.01073         21500       0.000107    2.30695
   22000      26.9       8.37    0.0898101   0.01073         22500       0.000214     4.8285
   23000     26.88       8.39    0.0900247   0.01073         24000       0.000321     7.7256
   25000     26.85       8.42    0.0903466   0.01073         25500       0.000107    2.73615
   26000     26.84       8.43    0.0904539   0.01073         26500       0.000107    2.84345
   27000     26.83       8.44    0.0905612   0.01073
```

Table.2. Surface area data and calculation of uncoated Bauxite (Mercury Porosimeter)

```
PS COATED BAUXITE   SAMPLE WT==0.25gm

PRESSURE  INTRUSION    CUM.     CUM.PORE    SYSTEM
                    INTRUSION    VOLUME    CONSTANT
=====================================================================================================

       4    31.67         0            0   0.01073

     7.1    31.22      0.45    0.0048285   0.01073                                                    SPECIFIC

    10.5    30.92      0.75    0.0080475   0.01073        AVE.                                TOTAL      SURFACE =TOTALP*DELTA V*0

    13.2    30.75      0.92    0.0098716   0.01073      PRESSURE    DELTA V    P*DELTA V   P*DELTA V     AREA

=====================================================================================================

    13.2    34.25      0.92    0.0098716   0.01073         56.6    0.000107    0.006073    69.76448    6.278803
     100    34.24      0.93    0.0099789   0.01073          150    0.001931     0.28971
     200    34.06      1.11    0.0119103   0.01073          250    0.018884      4.7212
     300     32.3      2.87    0.0307951   0.01073          350    0.011266    3.943275
     400    31.25      3.92    0.0420616   0.01073          450    0.006330    2.848815
     500    30.66      4.51    0.0483923   0.01073          625    0.006438     4.02375
     750    30.06      5.11    0.0548303   0.01073          875    0.002467    2.159412
    1000    29.83      5.34    0.0572982   0.01073         1500    0.002682     4.02375
    2000    29.58      5.59    0.0599807   0.01073         2500    0.000643      1.6095
    3000    29.52      5.65    0.0606245   0.01073         4000    0.000536       2.146
    5000    29.47       5.7     0.061161   0.01073         6250    0.000321    2.011875
    7500    29.44      5.73    0.0614829   0.01073         8750    0.000321    2.816625
   10000    29.41      5.76    0.0618048   0.01073        10500    0.000107     1.12665
   11000     29.4      5.77    0.0619121   0.01073        11500    0.000107     1.23395
   12000    29.39      5.78    0.0620194   0.01073        12500    0.000107     1.34125
   13000    29.38      5.79    0.0621267   0.01073        14000    0.000321      4.5066
   15000    29.35      5.82    0.0624486   0.01073        16250    0.000321    5.230875
   17500    29.32      5.85    0.0627705   0.01073        18750    0.000321    6.035625
   20000    29.29      5.88    0.0630924   0.01073        20500    0.000214      4.3993
   21000    29.27       5.9     0.063307   0.01073        21500    0.000107     2.30695
   22000    29.26      5.91    0.0634143   0.01073        22500    0.000214      4.8285
   23000    29.24      5.93    0.0636289   0.01073        24000    0.000107      2.5752
   25000    29.23      5.94    0.0637362   0.01073        25500    0.000107     2.73615
   26000    29.22      5.95    0.0638435   0.01073        26500    0.000107     2.84345
   27000    29.21      5.96    0.0639508   0.01073
```

Table.3. Surface area data and calculation of pps coated Bauxite (Mercury Porosimeter)

PB COATED BAUXITE SAMPLE WT==0.4572gm

| PRESSURE | INTRUSION | CUM. INTRUSION | CUM.PORE VOLUME | SYSTEM CONSTANT | AVE. PRESSURE | DELTA V | P*DELTA V | TOTAL P*DELTA V | SPECIFIC SURFACE =TOTALP*DELTA V*0 AREA |
|---|---|---|---|---|---|---|---|---|---|
| 3.7 | 32.02 | 0 | 0 | 0.01073 | | | | | |
| 6.6 | 31.44 | 0.58 | 0.0062234 | 0.01073 | | | | | |
| 9.3 | 30.94 | 1.08 | 0.0115884 | 0.01073 | | | | | |
| 13.2 | 30.48 | 1.54 | 0.0165242 | 0.01073 | | | | | |
| 13.3 | 32.98 | 1.54 | 0.0165242 | 0.01073 | 56.65 | 0.000107 | 0.006078 | 80.13503 | 3.943653 |
| 100 | 32.97 | 1.55 | 0.0166315 | 0.01073 | 150 | 0.012446 | 1.86702 | | |
| 200 | 31.81 | 2.71 | 0.0290783 | 0.01073 | 250 | 0.031117 | 7.77925 | | |
| 300 | 28.91 | 5.61 | 0.0601953 | 0.01073 | 400 | 0.029507 | 11.803 | | |
| 500 | 26.16 | 8.36 | 0.0897028 | 0.01073 | 625 | 0.012232 | 7.645125 | | |
| 750 | 25.02 | 9.5 | 0.101935 | 0.01073 | 875 | 0.004399 | 3.849387 | | |
| 1000 | 24.61 | 9.91 | 0.1063343 | 0.01073 | 1500 | 0.005686 | 8.53035 | | |
| 2000 | 24.08 | 10.44 | 0.1120212 | 0.01073 | 2500 | 0.001502 | 3.7555 | | |
| 3000 | 23.94 | 10.58 | 0.1135234 | 0.01073 | 4000 | 0.001073 | 4.292 | | |
| 5000 | 23.84 | 10.68 | 0.1145964 | 0.01073 | 6250 | 0.000429 | 2.6825 | | |
| 7500 | 23.8 | 10.72 | 0.1150256 | 0.01073 | 8750 | 0.000214 | 1.87775 | | |
| 10000 | 23.78 | 10.74 | 0.1152402 | 0.01073 | 10500 | 0.000107 | 1.12665 | | |
| 11000 | 23.77 | 10.75 | 0.1153475 | 0.01073 | 11500 | 0.000107 | 1.23395 | | |
| 12000 | 23.76 | 10.76 | 0.1154548 | 0.01073 | 12500 | 0.000107 | 1.34125 | | |
| 13000 | 23.75 | 10.77 | 0.1155621 | 0.01073 | 14000 | 0.000107 | 1.5022 | | |
| 15000 | 23.74 | 10.78 | 0.1156694 | 0.01073 | 16250 | 0.000107 | 1.743625 | | |
| 17500 | 23.73 | 10.79 | 0.1157767 | 0.01073 | 18750 | 0.000214 | 4.02375 | | |
| 20000 | 23.71 | 10.81 | 0.1159913 | 0.01073 | 20500 | 0.000107 | 2.19965 | | |
| 21000 | 23.7 | 10.82 | 0.1160986 | 0.01073 | 21500 | 0.000107 | 2.30695 | | |
| 22000 | 23.69 | 10.83 | 0.1162059 | 0.01073 | 22500 | 0.000107 | 2.41425 | | |
| 23000 | 23.68 | 10.84 | 0.1163132 | 0.01073 | 24000 | 0.000107 | 2.5752 | | |
| 25000 | 23.67 | 10.85 | 0.1164205 | 0.01073 | 25500 | 0.000107 | 2.73615 | | |
| 26000 | 23.66 | 10.86 | 0.1165278 | 0.01073 | 26500 | 0.000107 | 2.84345 | | |
| 27000 | 23.65 | 10.87 | 0.1166351 | 0.01073 | | | | | |

Table.4. Surface area data and calculation of ppb coated Bauxite (Mercury Porosimeter)

UNCOATED CARBONBLACKSAMPLE WT==0.1gm

| PRESSURE | INTRUSION | CUM. INTRUSION | CUM.PORE VOLUME | SYSTEM CONSTANT | AVE. PRESSURE | DELTA V | P*DELTA V | TOTAL P*DELTA V | SPECIFIC SURFACE =TOTALP*DELTA V*C AREA |
|---|---|---|---|---|---|---|---|---|---|
| 3.7 | 31.69 | 0 | 0 | 0.01073 | | | | | |
| 6.6 | 31.6 | 0.09 | 0.0009657 | 0.01073 | | | | | |
| 9.3 | 31.56 | 0.13 | 0.0013949 | 0.01073 | | | | | |
| 13.2 | 31.51 | 0.18 | 0.0019314 | 0.01073 | | | | | |
| 13.2 | 36.52 | 0.18 | 0.0019314 | 0.01073 | 81.6 | 0.001073 | 0.087556 | 510.6611 | 114.8987 |
| 150 | 36.42 | 0.28 | 0.0030044 | 0.01073 | 175 | 0.001180 | 0.206552 | | |
| 200 | 36.31 | 0.39 | 0.0041847 | 0.01073 | 250 | 0.003111 | 0.777925 | | |
| 300 | 36.02 | 0.68 | 0.0072964 | 0.01073 | 350 | 0.002575 | 0.90132 | | |
| 400 | 35.78 | 0.92 | 0.0098716 | 0.01073 | 450 | 0.001609 | 0.724275 | | |
| 500 | 35.63 | 1.07 | 0.0114811 | 0.01073 | 550 | 0.001931 | 1.06227 | | |
| 600 | 35.45 | 1.25 | 0.0134125 | 0.01073 | 650 | 0.001394 | 0.906685 | | |
| 700 | 35.32 | 1.38 | 0.0148074 | 0.01073 | 750 | 0.001609 | 1.207125 | | |
| 800 | 35.17 | 1.53 | 0.0164169 | 0.01073 | 850 | 0.001073 | 0.91205 | | |
| 900 | 35.07 | 1.63 | 0.0174899 | 0.01073 | 950 | 0.001180 | 1.121285 | | |
| 1000 | 34.96 | 1.74 | 0.0186702 | 0.01073 | 1500 | 0.008369 | 12.5541 | | |
| 2000 | 34.18 | 2.52 | 0.0270396 | 0.01073 | 2500 | 0.005472 | 13.68075 | | |
| 3000 | 33.67 | 3.03 | 0.0325119 | 0.01073 | 4000 | 0.009549 | 38.1988 | | |
| 5000 | 32.78 | 3.92 | 0.0420616 | 0.01073 | 6250 | 0.048285 | 301.7812 | | |
| 7500 | 28.28 | 8.42 | 0.0903466 | 0.01073 | 8750 | 0.005365 | 46.94375 | | |
| 10000 | 27.78 | 8.92 | 0.0957116 | 0.01073 | 10500 | 0.000965 | 10.13985 | | |
| 11000 | 27.69 | 9.01 | 0.0966773 | 0.01073 | 11500 | 0.000429 | 4.9358 | | |
| 12000 | 27.65 | 9.05 | 0.0971065 | 0.01073 | 12500 | 0.000429 | 5.365 | | |
| 13000 | 27.61 | 9.09 | 0.0975357 | 0.01073 | 14000 | 0.000643 | 9.0132 | | |
| 15000 | 27.55 | 9.15 | 0.0981795 | 0.01073 | 16250 | 0.000751 | 12.20537 | | |
| 17500 | 27.48 | 9.22 | 0.0989306 | 0.01073 | 18750 | 0.000536 | 10.05937 | | |
| 20000 | 27.43 | 9.27 | 0.0994671 | 0.01073 | 20500 | 0.000214 | 4.3993 | | |
| 21000 | 27.41 | 9.29 | 0.0996817 | 0.01073 | 21500 | 0.000214 | 4.6139 | | |
| 22000 | 27.39 | 9.31 | 0.0998963 | 0.01073 | 22500 | 0.000214 | 4.8285 | | |
| 23000 | 27.37 | 9.33 | 0.1001109 | 0.01073 | 24000 | 0.000536 | 12.876 | | |
| 25000 | 27.32 | 9.38 | 0.1006474 | 0.01073 | 25500 | 0.000214 | 5.4723 | | |
| 26000 | 27.3 | 9.4 | 0.100862 | 0.01073 | 26500 | 0.000214 | 5.6869 | | |
| 27000 | 27.28 | 9.42 | 0.1010766 | 0.01073 | | | | | |

Table.5. Surface area data and calculation of uncoated Carbon Black (Mercury Porosimeter)

PS COATEDCARBÖNBLACKSAMPLE WT==0.25gm

| PRESSURE | INTRUSION | CUM. INTRUSION | CUM.PORE VOLUME | SYSTEM CONSTANT | AVE. PRESSURE | DELTA V | P*DELTA V | TOTAL P*DELTA V | SPECIFIC SURFACE AREA =TOTALP*DELTA V* |
|---|---|---|---|---|---|---|---|---|---|
| 4.3 | 32.05 | 0 | 0 | 0.01073 | | | | | |
| 6.5 | 31.57 | 0.48 | 0.0051504 | 0.01073 | | | | | |
| 8.7 | 31.23 | 0.82 | 0.0087986 | 0.01073 | | | | | |
| 13.2 | 30.84 | 1.21 | 0.0129833 | 0.01073 | | | | | |
| 13.3 | 35.28 | 1.21 | 0.0129833 | 0.01073 | 56.65 | 0.003111 | 0.176277 | 1278.205 | 115.0384 |
| 100 | 34.99 | 1.5 | 0.016095 | 0.01073 | 150 | 0.01073 | 1.6095 | | |
| 200 | 33.99 | 2.5 | 0.026825 | 0.01073 | 300 | 0.016738 | 5.02164 | | |
| 400 | 32.43 | 4.06 | 0.0435638 | 0.01073 | 550 | 0.015773 | 8.675205 | | |
| 700 | 30.96 | 5.53 | 0.0593369 | 0.01073 | 800 | 0.007081 | 5.66544 | | |
| 900 | 30.3 | 6.19 | 0.0664187 | 0.01073 | 950 | 0.003004 | 2.85418 | | |
| 1000 | 30.02 | 6.47 | 0.0694231 | 0.01073 | 1500 | 0.024893 | 37.3404 | | |
| 2000 | 27.7 | 8.79 | 0.0943167 | 0.01073 | 2500 | 0.015129 | 37.82325 | | |
| 3000 | 26.29 | 10.2 | 0.109446 | 0.01073 | 3500 | 0.012554 | 43.93935 | | |
| 4000 | 25.12 | 11.37 | 0.1220001 | 0.01073 | 4500 | 0.014914 | 67.11615 | | |
| 5000 | 23.73 | 12.76 | 0.1369148 | 0.01073 | 6250 | 0.139704 | 873.1537 | | |
| 7500 | 10.71 | 25.78 | 0.2766194 | 0.01073 | 8750 | 0.013412 | 117.3593 | | |
| 10000 | 9.46 | 27.03 | 0.2900319 | 0.01073 | 10500 | 0.001502 | 15.7731 | | |
| 11000 | 9.32 | 27.17 | 0.2915341 | 0.01073 | 11500 | 0.000965 | 11.10555 | | |
| 12000 | 9.23 | 27.26 | 0.2924998 | 0.01073 | 12500 | 0.000643 | 8.0475 | | |
| 13000 | 9.17 | 27.32 | 0.2931436 | 0.01073 | 14000 | 0.000751 | 10.5154 | | |
| 15000 | 9.1 | 27.39 | 0.2938947 | 0.01073 | 16250 | 0.000536 | 8.718125 | | |
| 17500 | 9.05 | 27.44 | 0.2944312 | 0.01073 | 18750 | 0.000321 | 6.035625 | | |
| 20000 | 9.02 | 27.47 | 0.2947531 | 0.01073 | 20500 | 0.000214 | 4.3993 | | |
| 21000 | 9 | 27.49 | 0.2949677 | 0.01073 | 21500 | 0.000107 | 2.30695 | | |
| 22000 | 8.99 | 27.5 | 0.295075 | 0.01073 | 22500 | 0.000107 | 2.41425 | | |
| 23000 | 8.98 | 27.51 | 0.2951823 | 0.01073 | 24000 | 0.000107 | 2.5752 | | |
| 25000 | 8.97 | 27.52 | 0.2952896 | 0.01073 | 26000 | 0.000214 | 5.5796 | | |
| 27000 | 8.95 | 27.54 | 0.2955042 | 0.01073 | | | | | |

Table.6. Surface area data and calculation of pps coated Carbon Black (Mercury Porosimeter)

```
PB COATED CBLACK    SAMPLE WT==0.25gm

PRESSURE  INTRUSION   CUM.      CUM.PORE    SYSTEM
                   INTRUSION    VOLUME     CONSTANT
=============================================================================================================================

     4.3     32.57          0           0   0.01073

     6.5     32.43       0.14   0.0015022   0.01073                                                         SPECIFIC

     8.7     32.28       0.29   0.0031117   0.01073        AVE.                                    TOTAL      SURFACE =TOTALP*DELTA V*0

    13.2     32.12       0.45   0.0048285   0.01073      PRESSURE     DELTA V    P*DELTA V     P*DELTA V       AREA

=============================================================================================================================

    13.3     36.72       0.45   0.0048285   0.01073        56.65     0.001394    0.079021      1180.330     106.2297
     100     36.59       0.58   0.0062234   0.01073          150     0.007725     1.15884
     200     35.87        1.3    0.013949   0.01073          300     0.012446     3.73404
     400     34.71       2.46   0.0263958   0.01073          550     0.013841    7.612935
     700     33.42       3.75   0.0402375   0.01073          800     0.007832     6.26632
     900     32.69       4.48   0.0480704   0.01073          950     0.001931     1.83483
    1000     32.51       4.66   0.0500018   0.01073         1500     0.021567    32.35095
    2000      30.5       6.67   0.0715691   0.01073         2500     0.012554    31.38525
    3000     29.33       7.84   0.0841232   0.01073         3500     0.011803     41.3105
    4000     28.23       8.94   0.0959262   0.01073         4500     0.012554    56.49345
    5000     27.06      10.11   0.1084803   0.01073         6250     0.124038    775.2425
    7500      15.5      21.67   0.2325191   0.01073         8750     0.011910    104.2151
   10000     14.39      22.78   0.2444294   0.01073        10500     0.001287     13.5198
   11000     14.27       22.9    0.245717   0.01073        11500     0.000858      9.8716
   12000     14.19      22.98   0.2465754   0.01073        12500     0.000751     9.38875
   13000     14.12      23.05   0.2473265   0.01073        14000     0.000751     10.5154
   15000     14.05      23.12   0.2480776   0.01073        16250     0.000643    10.46175
   17500     13.99      23.18   0.2487214   0.01073        18750     0.000536    10.05937
   20000     13.94      23.23   0.2492579   0.01073        20500     0.000321     6.59895
   21000     13.91      23.26   0.2495798   0.01073        21500     0.000429      9.2278
   22000     13.87       23.3    0.250009   0.01073        22500     0.000429       9.657
   23000     13.83      23.34   0.2504382   0.01073        24000     0.000643     15.4512
   25000     13.77       23.4    0.251082   0.01073        25500     0.000321     8.20845
   26000     13.74      23.43   0.2514039   0.01073        26500     0.000214      5.6869
   27000     13.72      23.45   0.2516185   0.01073
```

Table.7. Surface area data and calculation of ppb coated Carbon Black (Mercury Porosimeter)

| SAMPLE (with following fillers) | PARTICLE SIZE nm | SURFACE AREA M**2/gm | HARDNESS SHORE A | ABRASION WEIGHT % LOSS | Tg C | Tan d | TENSILE STRENGTH MPa | ELONGATION AT BREAK % | C Content % |
|---|---|---|---|---|---|---|---|---|---|
| BAUXITE | 1500 | 6.6 | 50.5 | 19.2 | - 27.0 | 1.6 | 2.85∓0.12 | 240∓50 | 0.0 |
| PPS COATED BAUXITE (30 minutes) | -- | 6.3 | 49.0 | 18.6 | - 28.5 | 1.6 | 3.39∓0.15 | 290∓45 | 0.29∓0.3 |
| PPB COATED BAUXITE (26 minutes) | 5000 | 3.9 | 56.0 | -- | - 20.0 | 1.6 | 2.74∓0.59 | 240∓65 | 0.1∓0.3 |
| PPB COATED BAUXITE (8 minutes) | -- | -- | 54.0 | -- | - 23.9 | 1.35 | 3.0∓0.3 | 258∓33 | |
| CARBON BLACK | 20-25 | 114.9 | 66.0 | 7.8 | - 20.0 | 0.9 | 25.98∓3.91 | 639∓56 | |
| PPS COATED CARBON BLACK (30 minutes) | -- | 115.0 | 64.0 | 7.2 | - 19.5 | 0.9 | 27.73∓1.53 | 738∓42 | |
| PPB COATED CARBON BLACK (26 minutes) | -- | 106.2 | 67.0 | -- | - 28.0 | 0.9 | 17.68∓4.50 | 373∓72 | |
| PPB COATED CARBON BLACK (6 minutes) | -- | 116.0 | 66.0 | -- | - 17.8 | 0.72 | 23.05∓1.2 | 682∓29 | |
| PS COATED CASTING (0.16 gm) CARBON BLACK | -- | -- | 62-64 | -- | -- | -- | 21.69 | 615 | |
| PS COATED CASTING (0.24 gm) CARBON BLACK | -- | -- | 62-64 | -- | -- | -- | 15.4 | 419 | |
| SBR WITHOUT FILLER | -- | -- | 47.5-48 | -- | - 33.87 | 1.25 | 3.1 | 230 | |

Table.8. Complete data of SBR 1502 system

When Table 8 was investigated carefully it was observed that, there is a slight increase at the tensile strength value for pps coated bauxite filled vulcanizates while the reverse (slight decrease) is observed for the tensile strength of ppb coated bauxite filled samples. If we look at the % elongation values for these samples namely; uncoated, pps coated and ppb coated bauxite filled samples, we observe that there is a slight increase in pps coated one while there is no change in the ppb coated one.

If we look at the same properties; ie. tensile strength and % elongation of uncoated, pps coated, and ppb coated carbon blacks filled samples we observe that there are again slight increases in the tensile strength and % elongation values of pps coated carbon black filled sample. But if we look at the values of ppb coated carbon black filled sample we see that there exists a sudden decrease at both of the tensile strength and % elongation values.

On the other hand if we compare the hardness data for these samples we see a different and interesting behaviour.For example in the bauxite case we observe that pps coated bauxite filled samples are softer than the uncoated bauxite filled samples while the ppb coated bauxite filled samples are harder than the original one. For the carbon black case the same trend was observed, ie. if we assume the uncoated carbon black filled samples as original; the pps coated ones are softer while ppb coated ones are harder with respect to the original samples.

It will be useful to remember at this point that uncoated and pps coated bauxite and carbon black filled vulcanizates were also tested for their abrasion resistances. It was found from these tests that both of the pps coated bauxite and carbon black containing samples have lower abrasion losses than their uncoated references. Abrasion data is also included in Table 8.

Another important observation for these samples is that hardness values of the ppb coated bauxite filled samples are affected more than the tensile strength and % elongation values. The reverse was observed for carbon black case where tensile strength and % elongation values are much effected in the case of ppb coated carbon black filled samples where the hardness values are less affected.

When such an interesting behaviour has been detected the surface area data gained much importance. Because at the beginning the surface area measurements were only thought to be good proofs of the effectiveness of the coating process with respect to the plasma polymerization kinetics of styrene and butadiene. But with combination of the hardness and tensile strength data they have been started to be more explanatory for the kind of reinforcing mechanisms for both bauxite and carbon black relative to the kind of the coating they have.

When the Tg values of uncoated, pps coated and ppb coated filler used samples were compared it was observed that in each group Tg`s are very close to each other. As it is seen from Table 8 the Tg`s of uncoated and pps coated bauxite filled vulcanizates are -27 °C and -28.5 °C,respectively. In the carbon black case the Tg`s of the corresponding samples are -20 °C and -19.5 °C. But for the ppb coated samples of each group it was observed that this Tg difference is bigger. In addition to this reality it was also observed that Tg`s of the ppb coated bauxite filled samples (- 20 °C) are more positive than the original and pps coated samples.But the reverse was observed for the ppb coated carbon black samples (Tg = -28 °C) that is Tg`s for these samples are more negative than the original and pps coated ones. As a summary it was observed that Tg`s of uncoated and pps coated bauxite and carbon black filled samples are slightly equal to each other in their own groups. The Tg of ppb coated bauxite filled sample was increased to -20 °C, while that of carbon black filled sample was decreased to -28 °C.

When all of these results are put together it would be possible to make following speculations to explain the trend observed.

First of all because carbon black is high in structure and has a large surface area compared to bauxite it is very normal to get higher values of tensile strength and % elongation for carbon black filled vulcanizates than bauxite used ones.On the other hand it should be mentioned that both coatings, pps and ppb should increase the tensile strength of both carbon black and bauxite filled samples thermodynamically since due to the similar surfaces of both matrix and filler surface, solubility parameters of both matrix and filler surface will be near to each other. In this case $\Delta H_{mix}$ will approach to zero and $\Delta G_{mix}$ will start to decrease which induces the compatibility between the filler surface and matrix that is increased adhesion [43]. But one should be very carefull that there are two important parameters involved here, namely selectivity of the filler surfaces to the matrix and the total surface area of fillers to be wetted by the polymeric matrix, SBR. As it was mentioned earlier carbon black is a very good reinforcing filler because of its porous structure and high surface area. But when the surface area has been decreased as in the case of ppb coating from 114.9 $m^2/g$ to 106.2 $m^2/g$ it looses part of its reinforcing effect. That is the reason of decreasing the tensile strength of carbon black filled samples from 26 MPa to 18 MPa due to the ppb coating (the decrease is 32 %). When reinforcing has been decreased to such extent it is very normal for the whole system to behave like a lower crosslinked one and that explains the decrease of the Tg value from -20 $^oC$ to -28 $^oC$ due to the ppb coating.

But bauxite system is different than carbon black where the structure is not enhancing the physical adhesion and total surface area is very low for reinforcing purposes. For this reason the sudden decrease of specific surface area of bauxite due to ppb coating does not affect the tensile strength and % elongation much. But in this case another parameter becomes to predominate: the selectivity of the filler surface due to ppb coating. One should remember that the SBR matrix used contains 23.5 % styrene and 76.5 % butadiene. At the same time the filler surface has been coated with ppb which selectively adheres to the butadiene parts of the matrix. In addition to this, the thickness of the ppb coat on the bauxite surface is thicker than the one on carbon black due to the large differences of their surface areas. When the non-reinforcing effect of bauxite because of its shapeless and non-porous structure is added to the above points it becomes easy to understand why the hardness of the ppb coated bauxite used samples suddenly jumpes from 50.5 to 56 (Shore A) while its tensile strength and % elongation are not changing considerably as mentioned before.

To support the thickness increase due to ppb coatings of bauxite some new particle size determination experiments were carried out at this stage and it was seen that the particle size of ppb coated samples are around 5000 nm where the original bauxite has a particle size as 1500 nm as an average. The results of these particle size determination tests can be seen in Figures 22-25.

The same selectivity factor is playing role for the carbon black case too;but because of the thinness of the ppb coat due to the large surface area of carbon black and the loss in reinforcing; selectivity factor looses its dominancy and that is why the hardness of the ppb coated carbon black filled sample is not inreasing as in the case of bauxite, although the trend is preserved.

As a summary, there are two main parameters : 1- Selectivity and 2- Surface area. Selectivity has a dominancy in the case of bauxite and responsible from the large increase of hardness due to the ppb coating. Surface area has a dominancy in the case of carbon black and is responsible from the decrease in reinforcing.

After having these observations for the ppb coated samples, the effect of coating thickness was tried to be investigated. For this purpose two sets of experiments were designed. In one of these experiments bauxite was coated with ppb for 8.0 minutes under the same conditions. In the second experiment carbon black was coated with ppb again under the same conditions. The results of these tests were very similar with that of the uncoated samples. Although these tests supported the previous explanations, the effect of coating thickness couldn`t be seen clearly because the coats were very thin. The results of these tests are given in Figures 26-27 and also tabulated in Table 8.

Later on another experiment was designed to see the thickness effect of coating. For this purpose 0.16 g polystyrene having a molecular weight of 10 000 ($M_w$), was coated to the carbon black surface from ether solution. The hardness and the tensile strength of the sample prepared by this way was 62-64 Shore A and 21.5 MPa respectively. Then the same procedure was repeated with 0.24 g of the same polystyrene and this time tensile strength has been decreased to 15.5 MPa while the hardness was same. Since the samples became softer due to the thicker coating and the trend for the hardness is preserved, the proposed explanation for the selectivity effect was supported. On the other hand the great decreases in tensile strength have supported the surface area effect suggestion strongly. In addition to this the advantage of plasma coating technique over the solution casting coating technique have been seen clearly once more.

It should also be mentioned at this point that when table 8 has been investigated carefully one additional column is seen for the tan $\delta$ values of the above compounds. It is clearly seen that tan $\delta$`s are the same in each group and have the values of 1.6 and 0.9 for bauxite and carbon black (surface untreated and

```
<PARTICLE SIZE DISTRIBUTION DATA>

     DIAM.        TIME      ABS. CHANGE  CUM
     (µm)                        (%)   (R %)

01  80.000 G 0:00:02   0.987              0
02  60.000 G 0:00:04   0.987      1·1     1.1
03  50.000 G 0:00:05   0.987      1·2     2.3
04  40.000 G 0:00:08   0.986      1·5     3.8
05  30.000 G 0:00:15   0.984      2·5     6.3
06  20.000 G 0:00:33   0.979      5·0    11.4
07  15.000 G 0:00:59   0.972      5·1    16.5
08  10.000 G 0:02:13   0.952     11·3    27.8
09   8.000 G 0:03:28   0.938      5·5    33.3
10   6.000 G 0:06:10   0.908      8·6    41.9
11   5.000 G 0:08:52   0.877      7·1    49.0
12   4.000 G 0:13:51   0.840      6·9    55.8
13   3.000 C 0:00:54   0.809      4·2    60.0
14   2.000 C 0:01:42   0.664     11·4    71.4
15   1.500 C 0:02:33   0.567      5·4    76.9
16   1.000 C 0:04:13   0.403      7·1    84.0
17   0.800 C 0:05:26   0.289      4·4    88.4
18   0.600 C 0:07:19   0.166      4·5    92.9
19   0.500 C 0:08:44   0.128      1·4    94.2
20   0.400 C 0:10:45   0.084      1·6    95.9
21   0                 0          4·1   100.0
```

```
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 SAMPLE ID   PPB-BOKSIT
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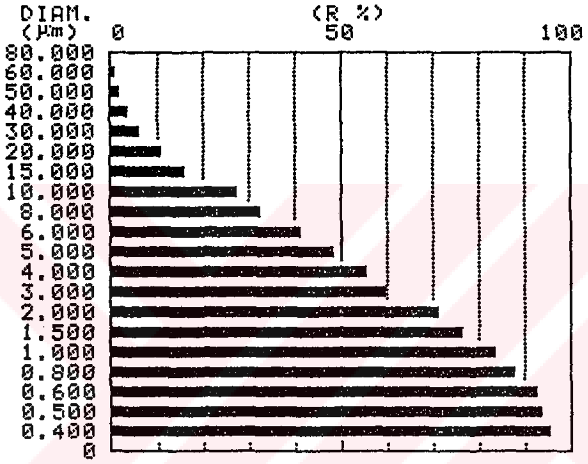

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<SA-CP3 DIFFERENTIAL GRAPH>

 SAMPLE ID   PPB-BOKSIT
 SAMPLE #    1
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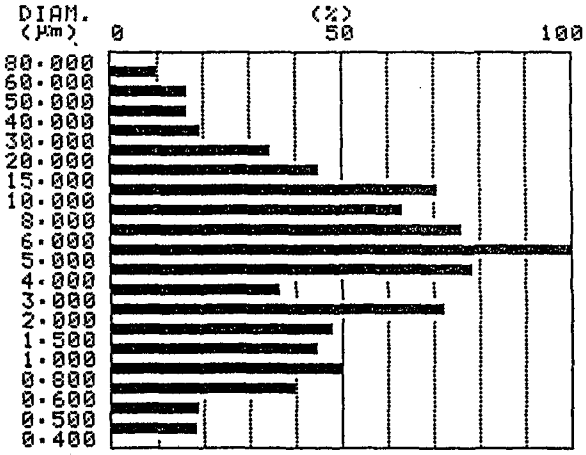


Figure.22. Particle size distribution data of PPB coated bauxite. Sample # 1.

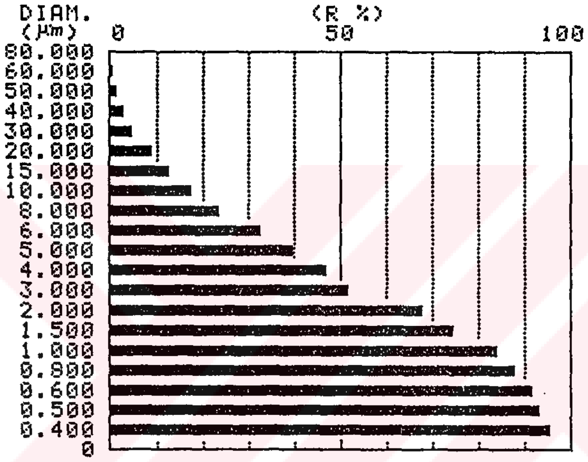
```
<PARTICLE SIZE DISTRIBUTION DATA>

      DIAM.       TIME     ABS. CHANGE  CUM
      (µm)                       (%)   (R %)

01  80.000 G 0:00:02  1.000              0
02  60.000 G 0:00:04  0.999    0.9      0.9
03  50.000 G 0:00:05  0.999    1.0      1.9
04  40.000 G 0:00:08  0.998    1.2      3.0
05  30.000 G 0:00:15  0.997    2.0      5.0
06  20.000 G 0:00:33  0.994    4.0      9.1
07  15.000 G 0:00:59  0.989    4.1     13.2
08  10.000 G 0:02:13  0.981    4.6     17.7
09   8.000 G 0:03:28  0.966    6.2     23.9
10   6.000 G 0:06:10  0.938    9.1     33.0
11   5.000 G 0:08:52  0.910    7.1     40.1
12   4.000 G 0:13:51  0.874    7.4     47.6
13   3.000 C 0:00:54  0.841    4.8     52.4
14   2.000 C 0:01:42  0.661   15.8     68.2
15   1.500 C 0:02:33  0.553    6.7     74.8
16   1.000 C 0:04:13  0.353    9.7     84.5
17   0.800 C 0:05:26  0.264    3.8     88.3
18   0.600 C 0:07:19  0.170    3.8     92.1
19   0.500 C 0:08:44  0.133    1.5     93.6
20   0.400 C 0:10:45  0.071    2.5     96.1
21   0                0        3.9    100.0
```

<SA-CP3 CUMULATIVE GRAPH>

SAMPLE ID   PPB-BOKSIT
SAMPLE #    2



<SA-CP3 DIFFERENTIAL GRAPH>

SAMPLE ID   PPB-BOKSIT
SAMPLE #    2

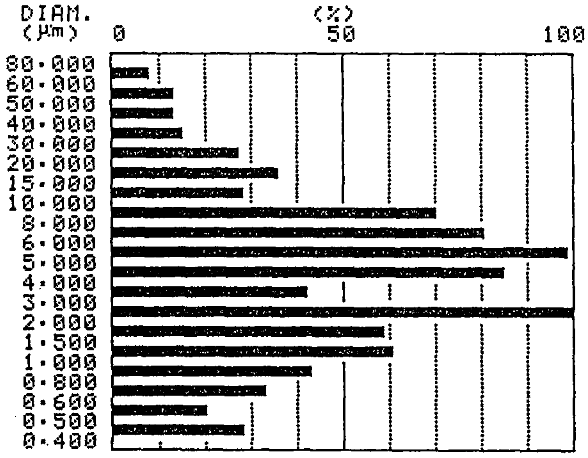


Figure.23. Particle size distribution data of PPB coated bauxite. Sample # 2.

```
<PARTICLE SIZE DISTRIBUTION DATA>

      DIAM.          TIME      ABS.  CHANGE   CUM
      (µm)                              (%)   (R %)

01   80.000 G  0:00:02   0.982              0
02   60.000 G  0:00:04   0.982    1.5       1.5
03   50.000 G  0:00:05   0.981    1.2       2.7
04   40.000 G  0:00:08   0.980    1.9       4.6
05   30.000 G  0:00:14   0.977    3.3       7.9
06   20.000 G  0:00:32   0.971    6.5      14.4
07   15.000 G  0:00:58   0.961    6.6      21.0
08   10.000 G  0:02:09   0.938   12.1      33.1
09    8.000 G  0:03:22   0.920    6.0      39.1
10    6.000 G  0:06:00   0.885    9.1      48.2
11    5.000 G  0:08:38   0.862    5.0      53.2
12    4.000 G  0:13:29   0.808    9.1      62.3
13    3.000 C  0:00:53   0.774    4.1      66.4
14    2.000 C  0:01:40   0.671    7.5      73.8
15    1.500 C  0:02:30   0.589    4.2      78.0
16    1.000 C  0:04:09   0.399    7.5      85.6
17    0.800 C  0:05:21   0.277    4.3      89.8
18    0.600 C  0:07:13   0.207    2.3      92.1
19    0.500 C  0:08:37   0.139    2.2      94.3
20    0.400 C  0:10:37   0.085    1.8      96.2
21    0                  0        3.8     100.0
```

```
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 SAMPLE ID   PPB BOKSIT
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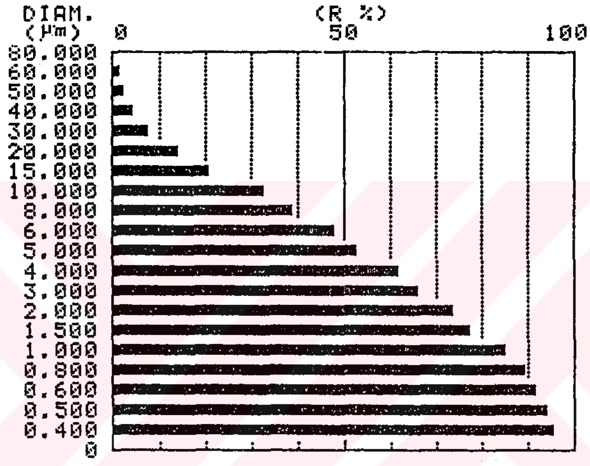

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<SA-CP3 DIFFERENTIAL GRAPH>

 SAMPLE ID   PPB BOKSIT
 SAMPLE #    3
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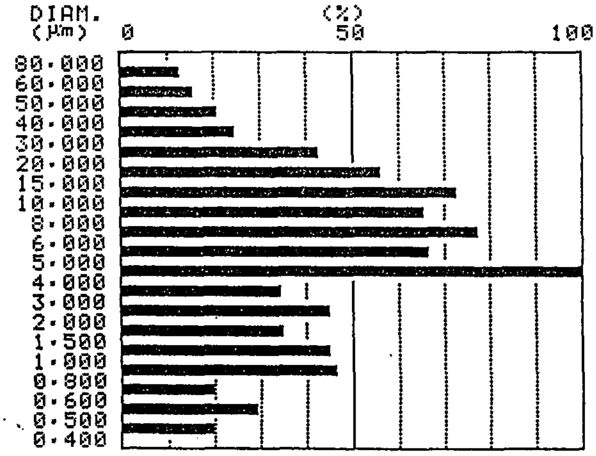


Figure.24. Particle size distribution data of PPB coated bauxite. Sample # 3.

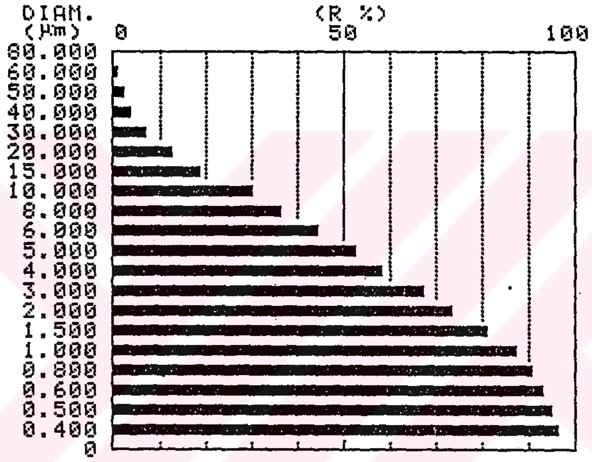
```
<PARTICLE SIZE DISTRIBUTION DATA>

      DIAM.       TIME     ABS.  CHANGE   CUM
      (μm)                        (%)    (R %)

01   80.000 G 0:00:02  1.000              0
02   60.000 G 0:00:04  1.000       1.4    1.4
03   50.000 G 0:00:05  0.999       1.1    2.5
04   40.000 G 0:00:08  0.998       1.8    4.3
05   30.000 G 0:00:14  0.996       3.0    7.3
06   20.000 G 0:00:32  0.989       6.0   13.2
07   15.000 G 0:00:58  0.980       6.1   19.3
08   10.000 G 0:02:09  0.957      11.6   30.9
09    8.000 G 0:03:22  0.938       6.0   36.8
10    6.000 G 0:06:00  0.907       8.1   44.9
11    5.000 G 0:08:38  0.866       8.3   53.2
12    4.000 G 0:13:29  0.830       5.8   59.0
13    3.000 C 0:00:53  0.752       9.0   68.0
14    2.000 C 0:01:40  0.665       6.1   74.1
15    1.500 C 0:02:30  0.507       7.7   81.9
16    1.000 C 0:04:09  0.351       6.0   87.8
17    0.800 C 0:05:21  0.246       3.5   91.3
18    0.600 C 0:07:13  0.182       2.1   93.4
19    0.500 C 0:08:37  0.109       2.3   95.7
20    0.400 C 0:10:37  0.070       1.3   97.0
21    0                0           3.0  100.0
```

<SA-CP3 CUMULATIVE GRAPH>

SAMPLE ID   PPB BOKSIT
SAMPLE #    4



<SA-CP3 DIFFERENTIAL GRAPH>

SAMPLE ID   PPB BOKSIT
SAMPLE #    4

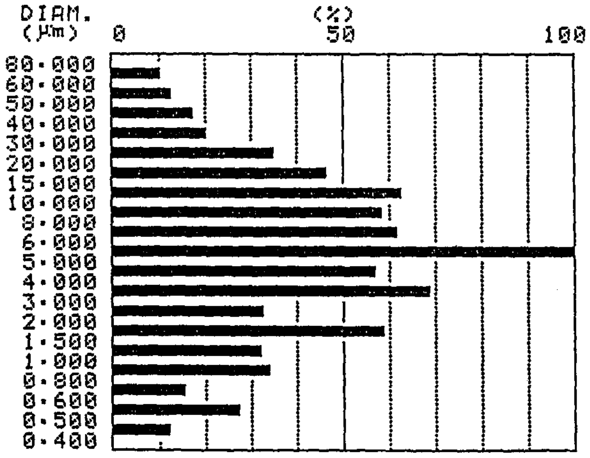


Figure.25. Particle size distribution data of PPB coated bauxite. Sample # 4.

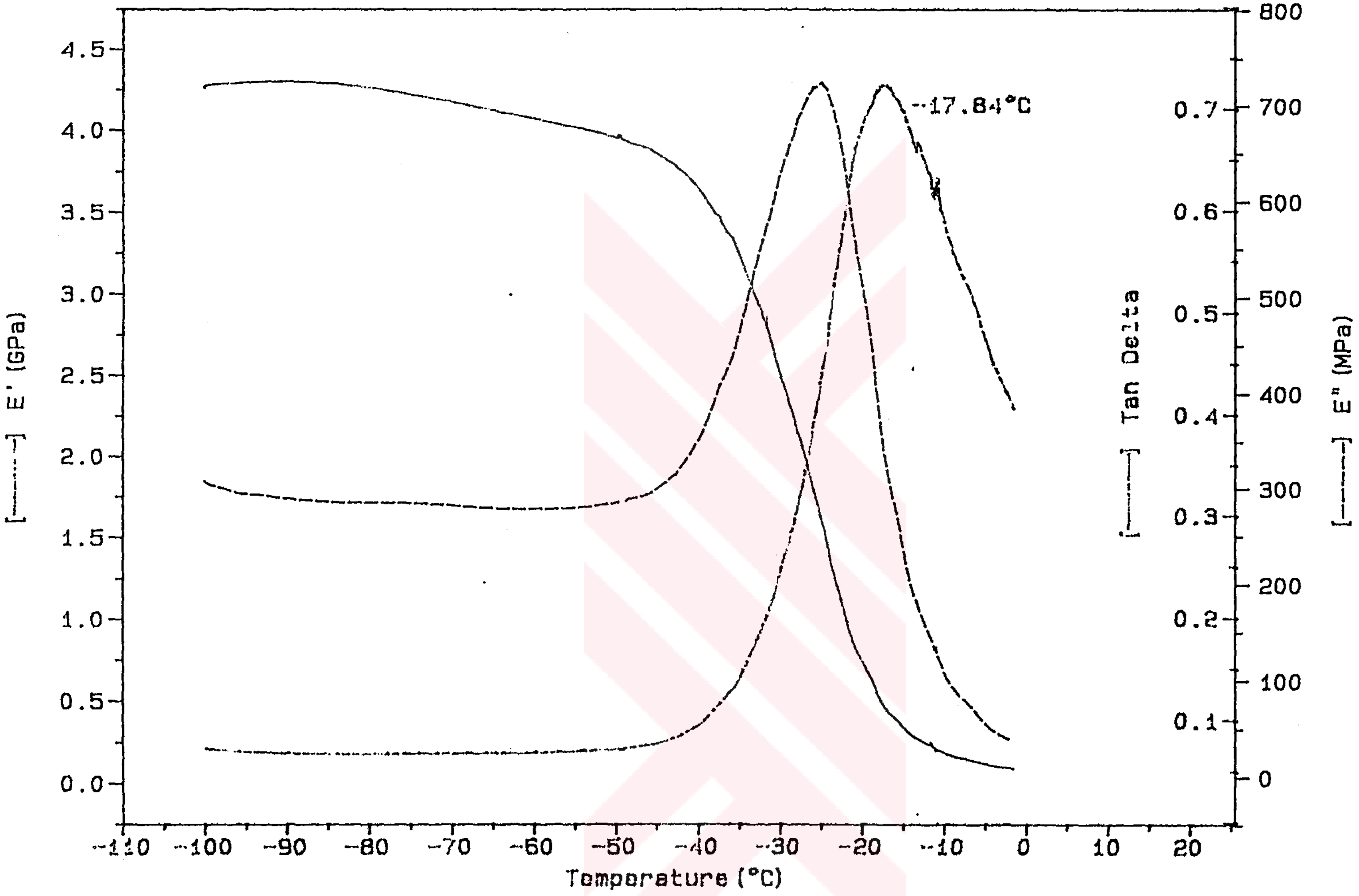


Figure.26. DMA of 6 min. PPB coated carbon black filled SBR 1502 vulcanizate.

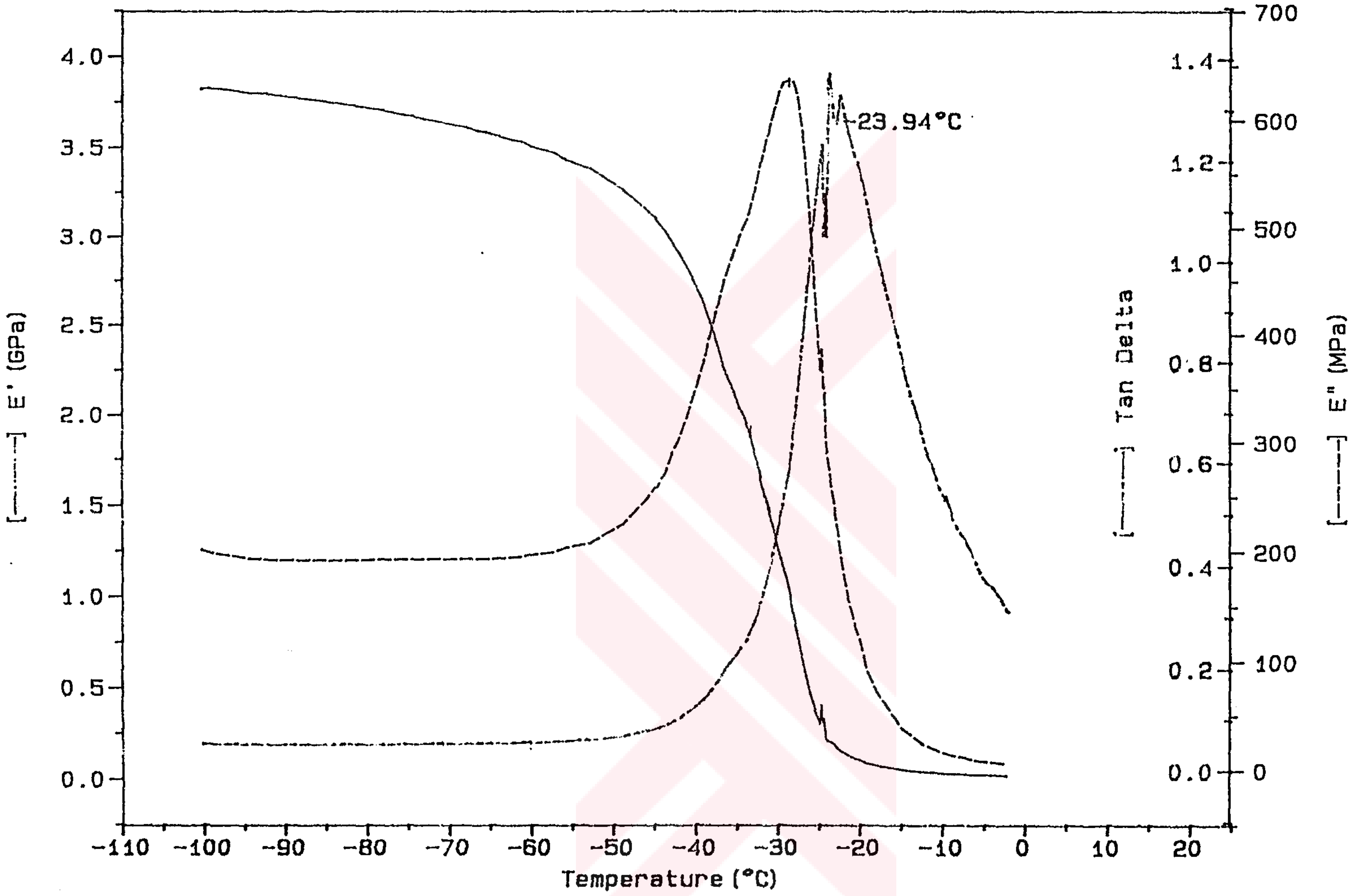


Figure.27. DMA of 8 min. PPB coated bauxite filled SBR 1502 vulcanizate.

treated) respectively. These results give us an additional information that is bauxite filled samples have higher heat buildups than the carbon black filled samples under dynamic conditions.

It is known from literature that carbon black surfaces have important effects such as changing the cure kinetics during the curing reactions [45,46]. To check the existency of such an event the carbon black group compounds were tested for their rheometric attitudes. The tests done at 191 °C with a Monsanto rheometer showed that pps coated samples are vulcanizing faster while the ppb coated ones are curing slower. But when the same tests were repeated at 175 °C the difference in curing rates disappear. So it was concluded that although there is a possibility of the vulcanization kinetics effect, it is small. The results of these rheometry studies are given in Figures 28-30.

The data collected up to this point was related for 35 phr filler loading with respect to 100 phr rubber (phr = parts per hundred rubber). At this point some new compounds were prepared to understand the trends of hardness, tensile strength, and % elongation with respect to the different parts of loadings. The results of these tests together with the previous ones are given in figures 31-36. These figures include the results of the samples containing different parts of fillers, the effect of different coating techniques, and the data belong to the sample which contains no filler as a reference all together.

Although all data collected to this point were consistent with each other and with the explanation for the importance of two factors; 1-selectivity, and 2-surface area, electron microscopy studies were also realized as mentioned in the experimental part.

This study was done to investigate the fracture surfaces of the vulcanizates which would probably reflect only the differences of the surface patterns of each sample individually due to the surface treatment of fillers. But fortunately the photographs obtained from electron microscope gave satisfactory visual information about the quality of adhesion which supported the results of the mechanical tests described above.These photographs are given in Figures 37-42.

As it can be seen figure 37 and 38 there is not a satisfactory indication of adhesion on the normal and pps coated bauxite samples, ie. filler particles seem to come out from the matrix. But when the photograph of ppb coated sample was investigated from figure 39 a very different surface pattern was observed. In this photograph it is clearly seen that filler particles are strongly adhered to the rubber matrix which proves the selectivity of the filler surface to the

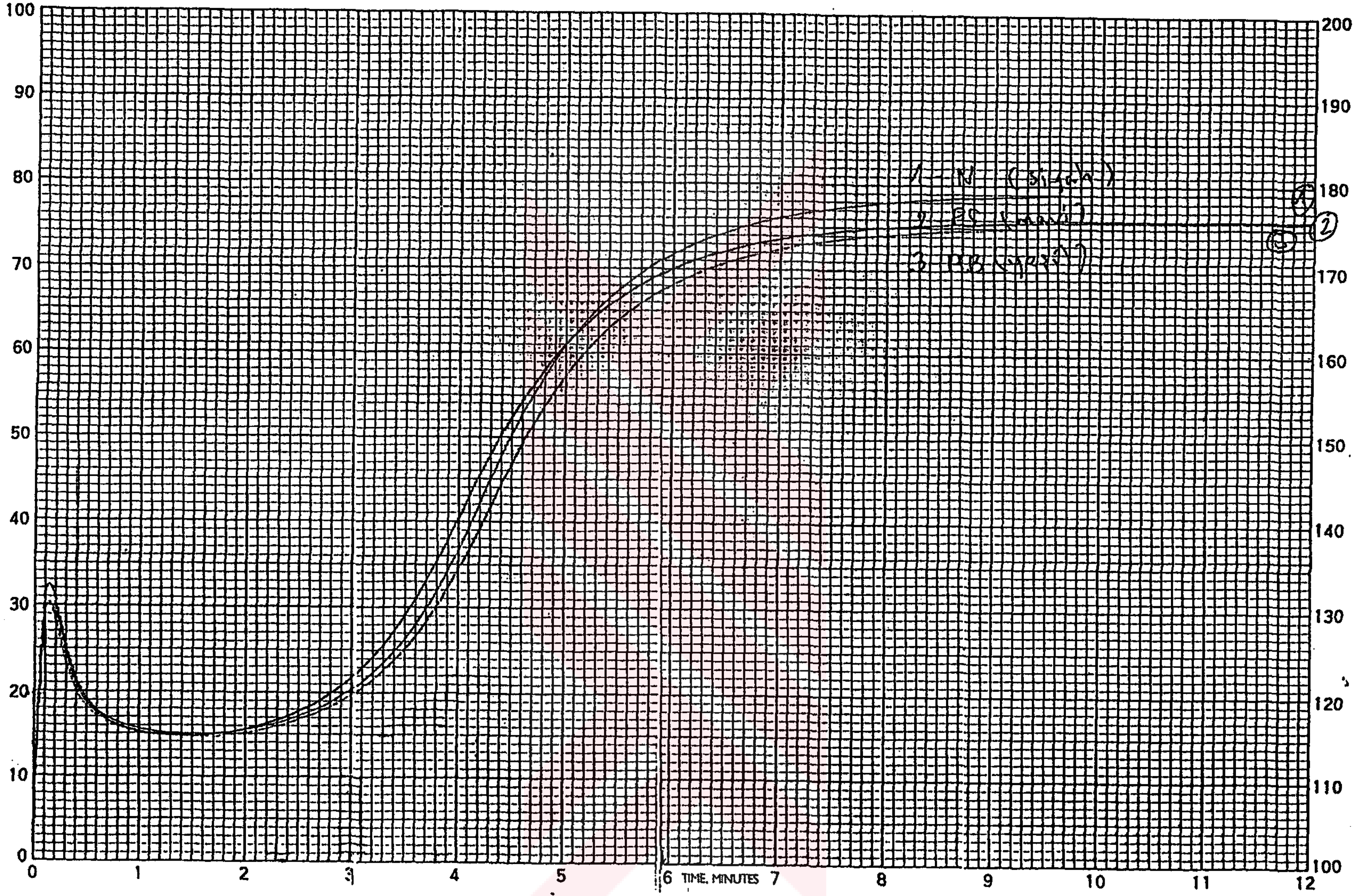


Figure 28. Rheometric attitudes of uncoated, PPS coated, PPB coated carbon blacl filled final batch compounds.(191 °C )

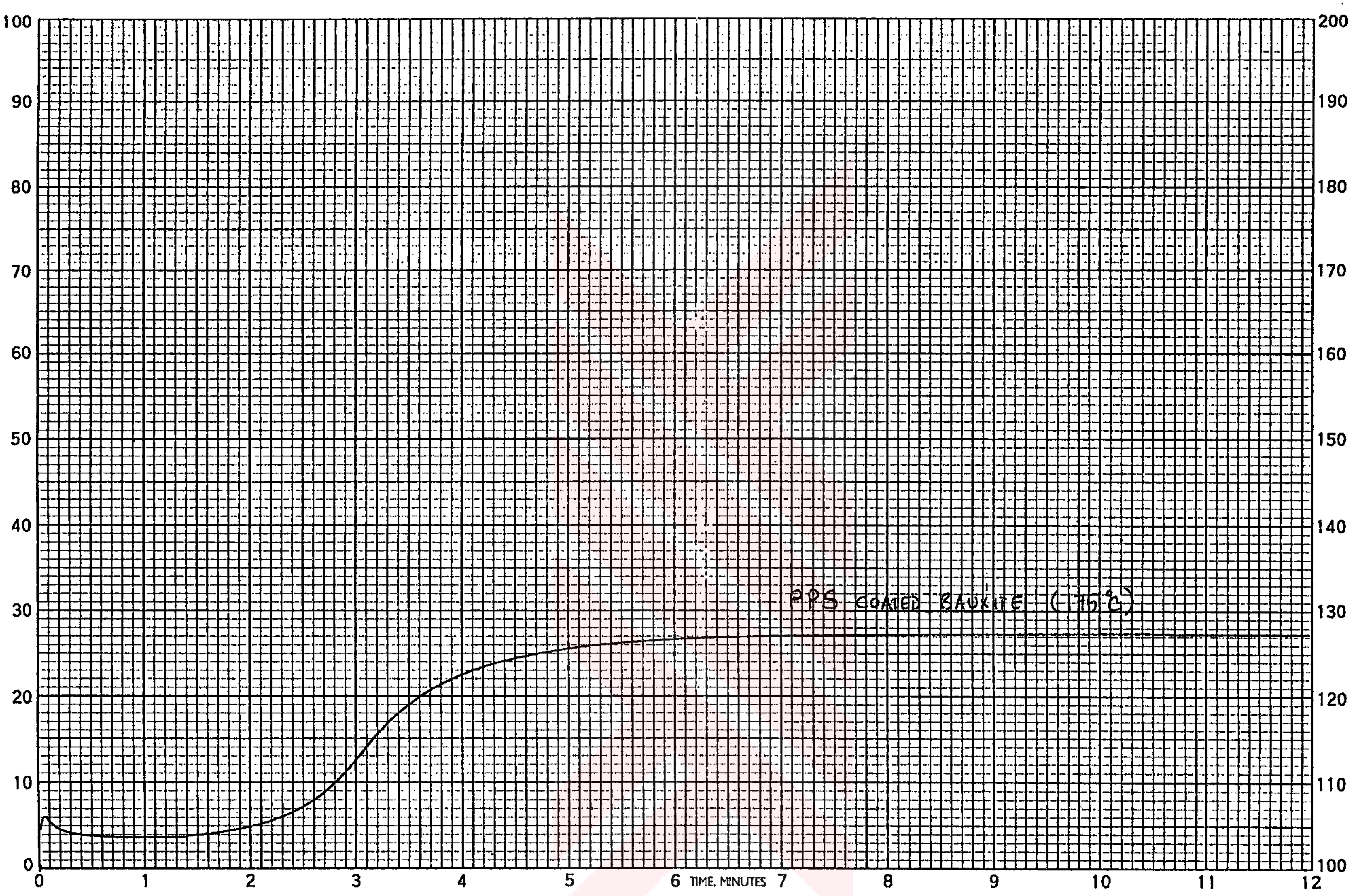


Figure.29. Rheometric attitude of PPS coated bauxite filled final batch compound. ( 175 °C )

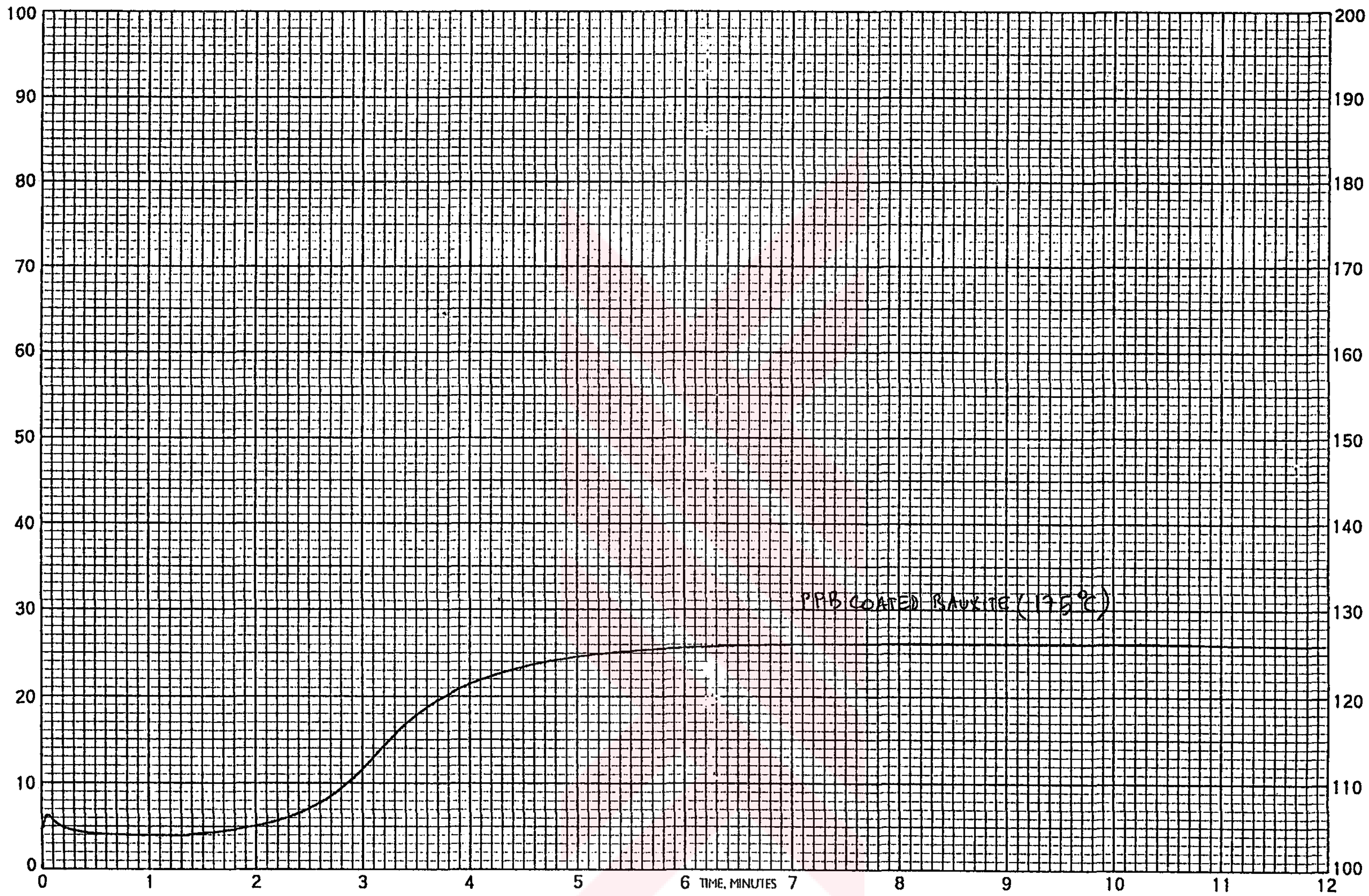


Figure.30. Rheometric attitude of PPB coated bauxite filled final batch compound. ( 175 °C )

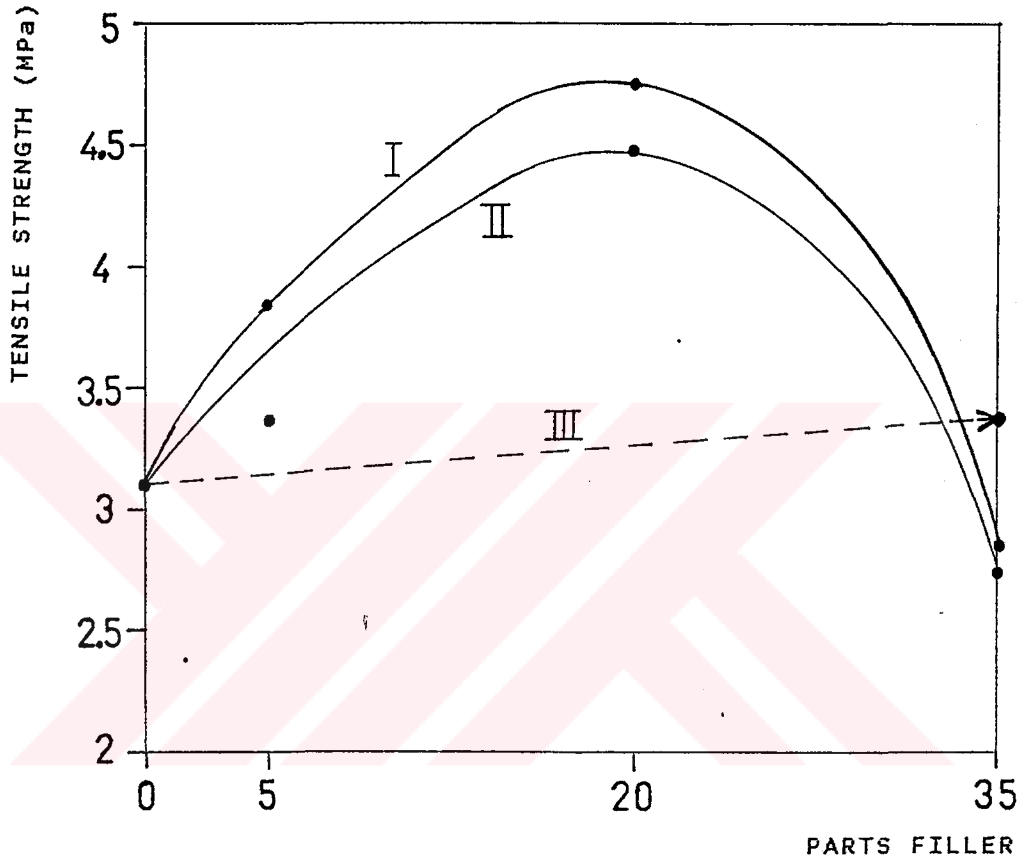


Figure 31. Tensile strength vs. parts filler for bauxite system.
I=uncoated, II=ppb coated, III=pps coated

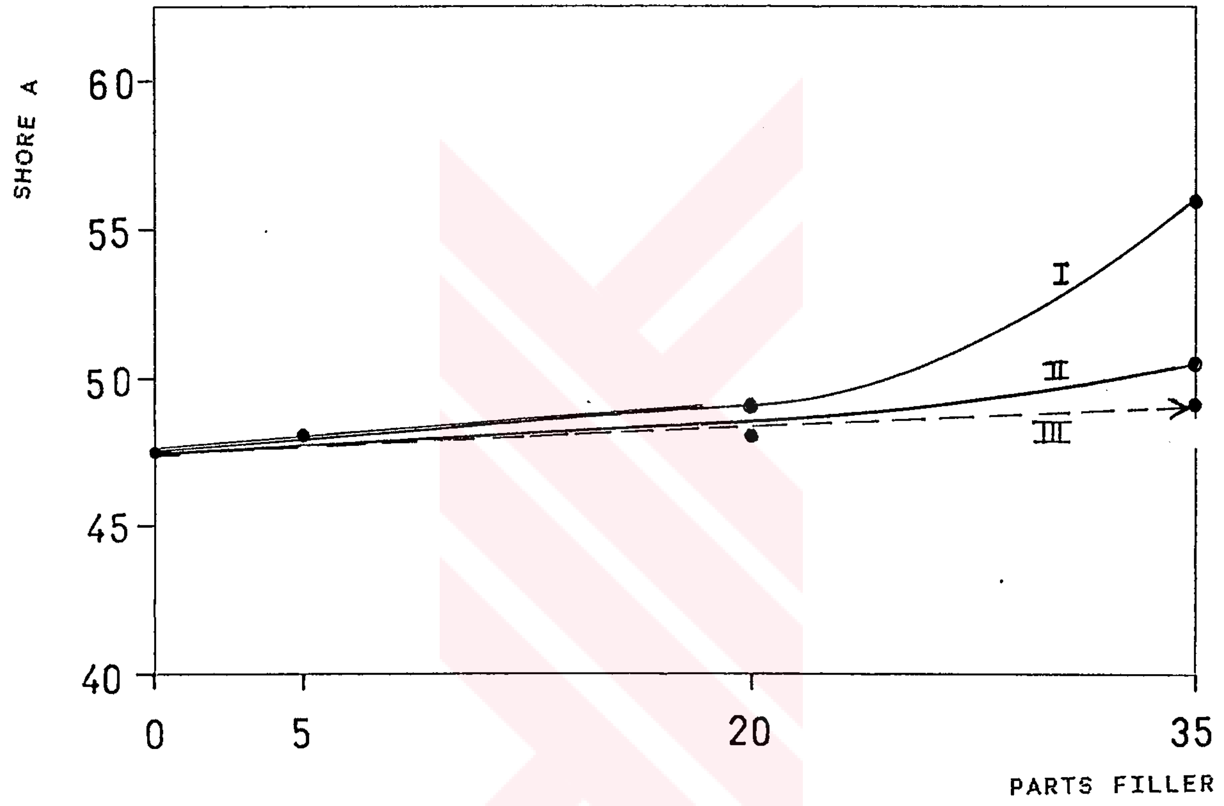


Figure 32. Hardness vs. parts filler for bauxite system.
I=ppb coated, II=uncoated, III=pps coated

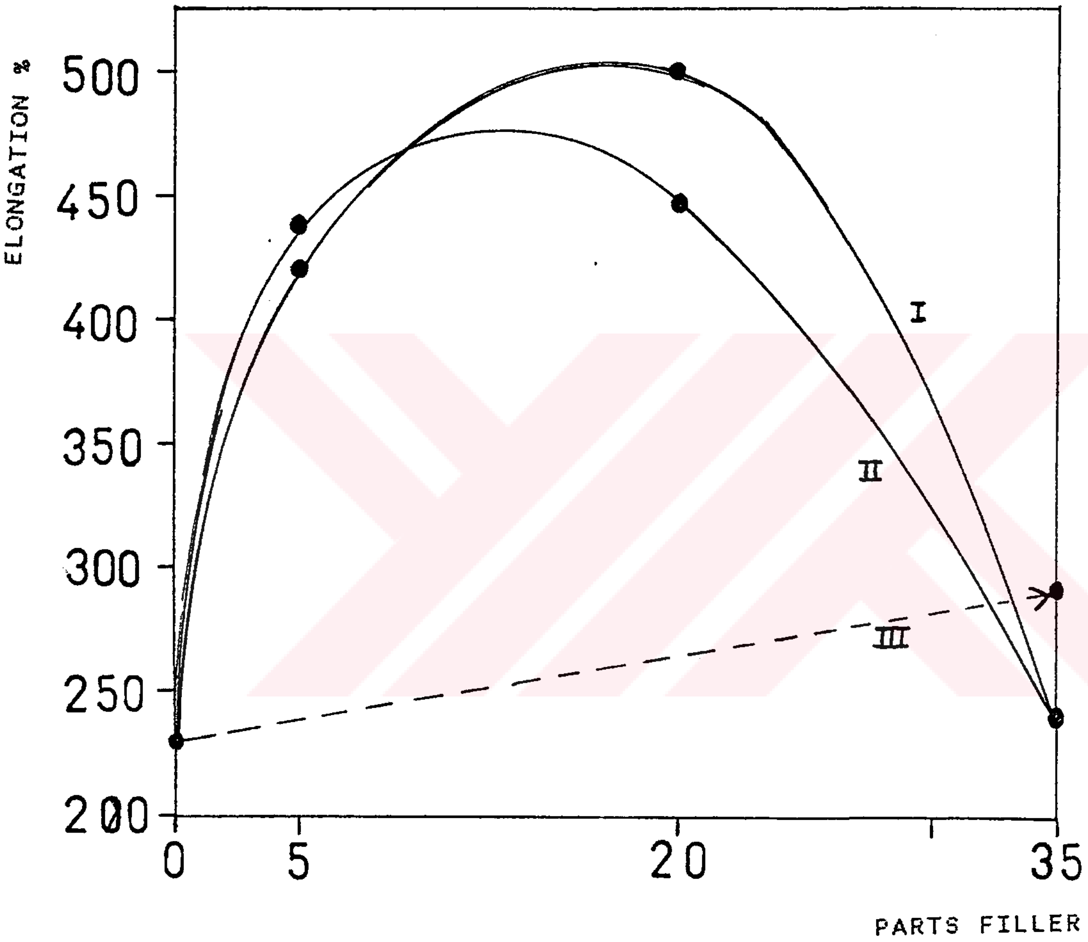


Figure 33. % Elongation vs. parts filler for bauxite system.
I=uncoated, II=ppb coated, III=pps coated

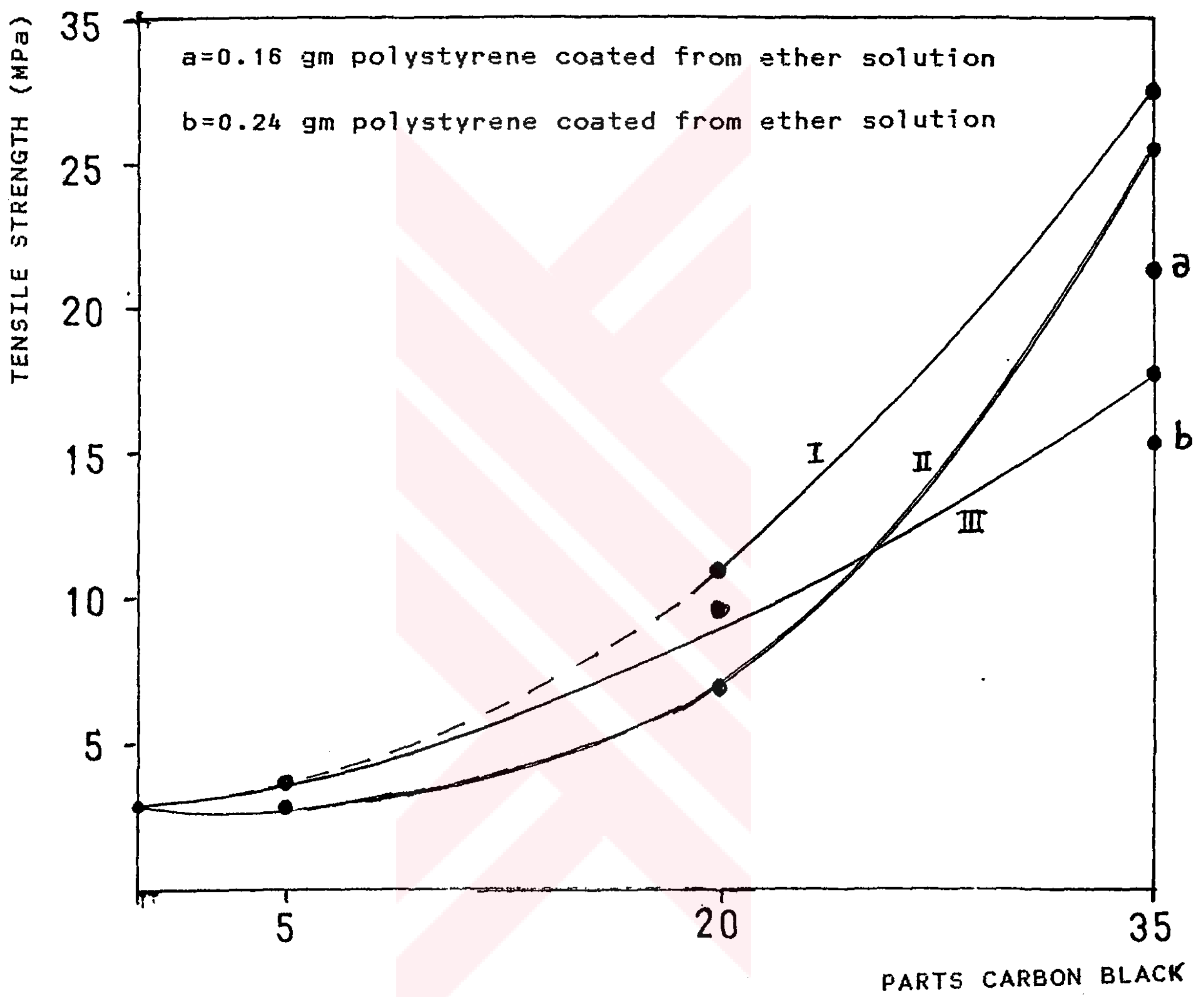


Figure 34. Tensile strength vs. parts filler for carbon black system,( tensile strengths of solution casting data are also included)
I=pps coated, II=uncoated, III=ppb coated

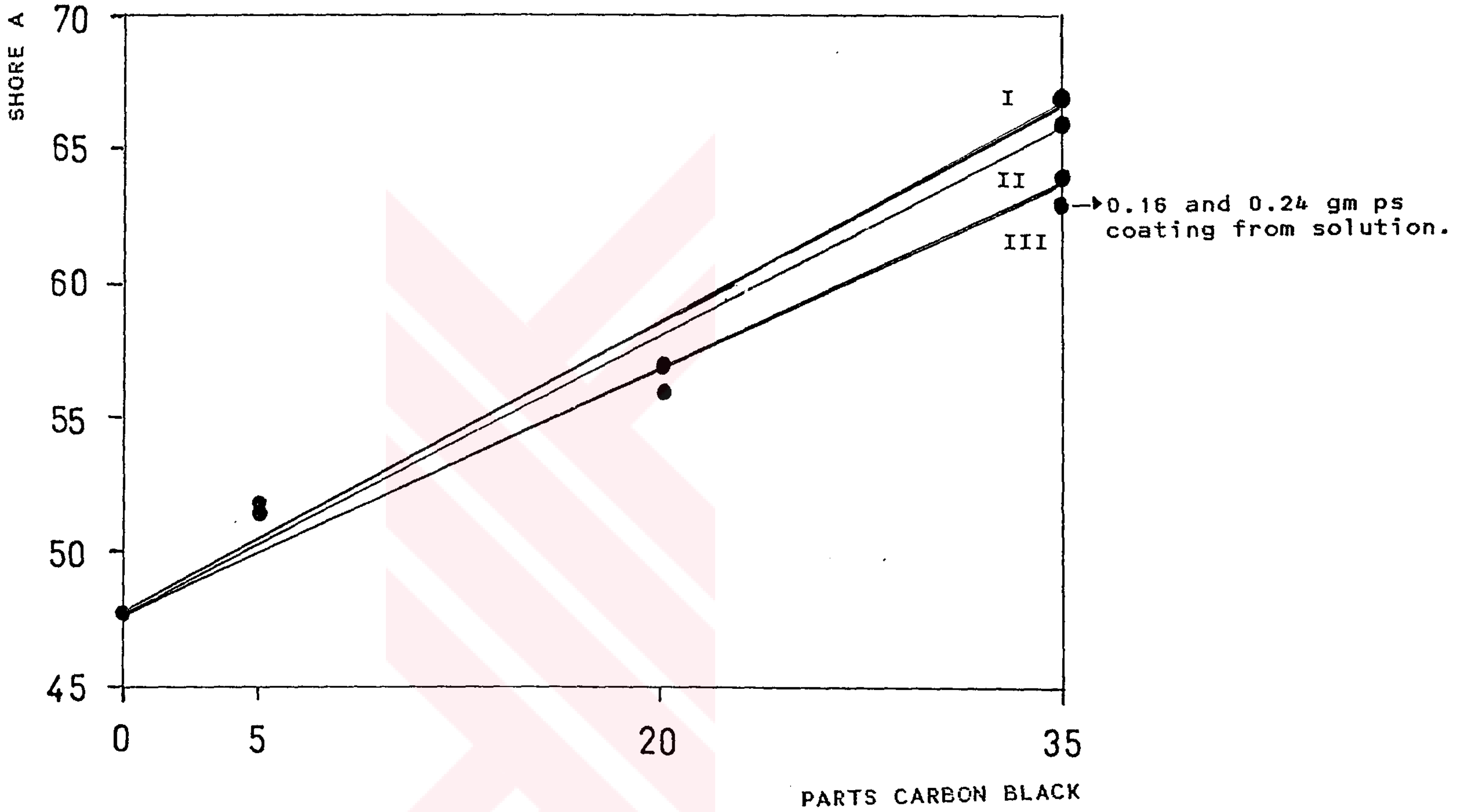


Figure.35. Hardness vs. parts carbon black, (hardness` of solution casting data are also included).
I=ppb coated, II=uncoated, III=pps coated

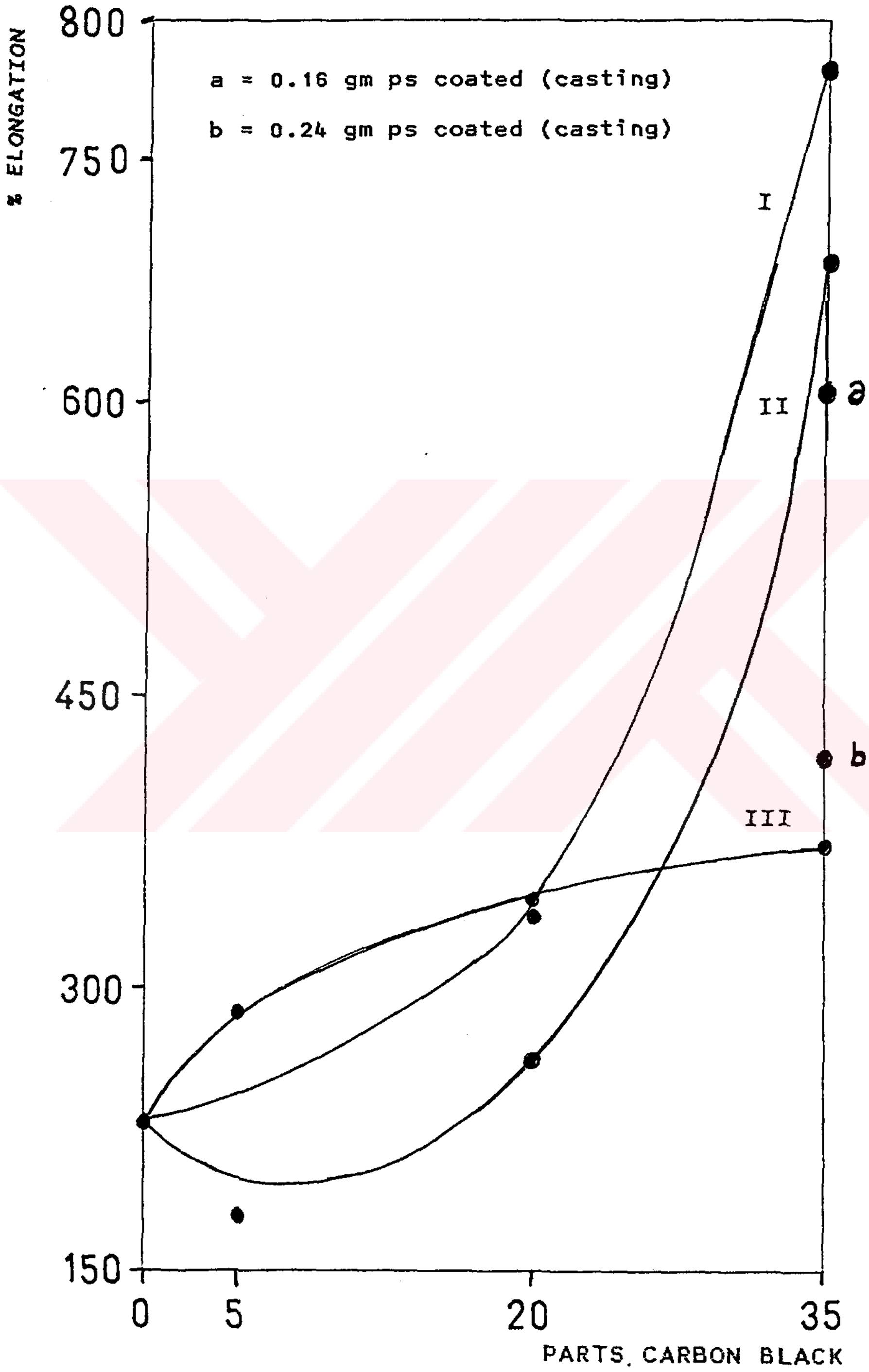
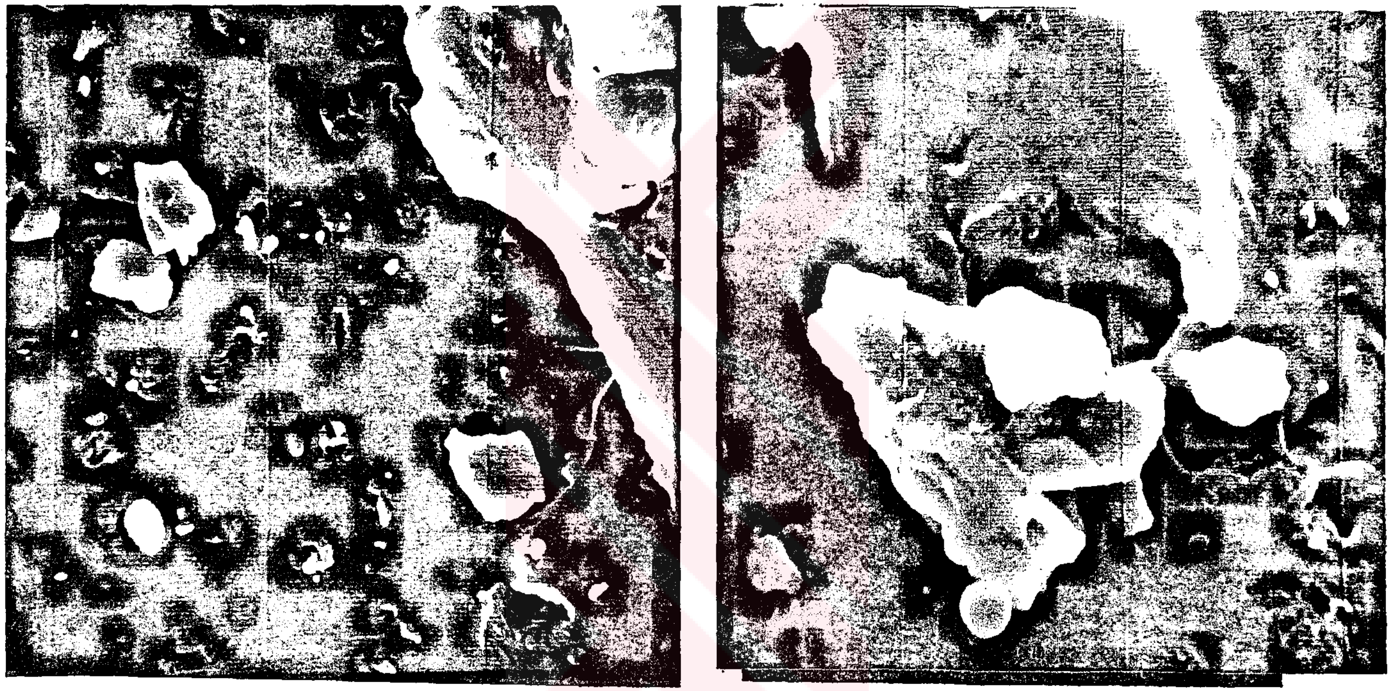


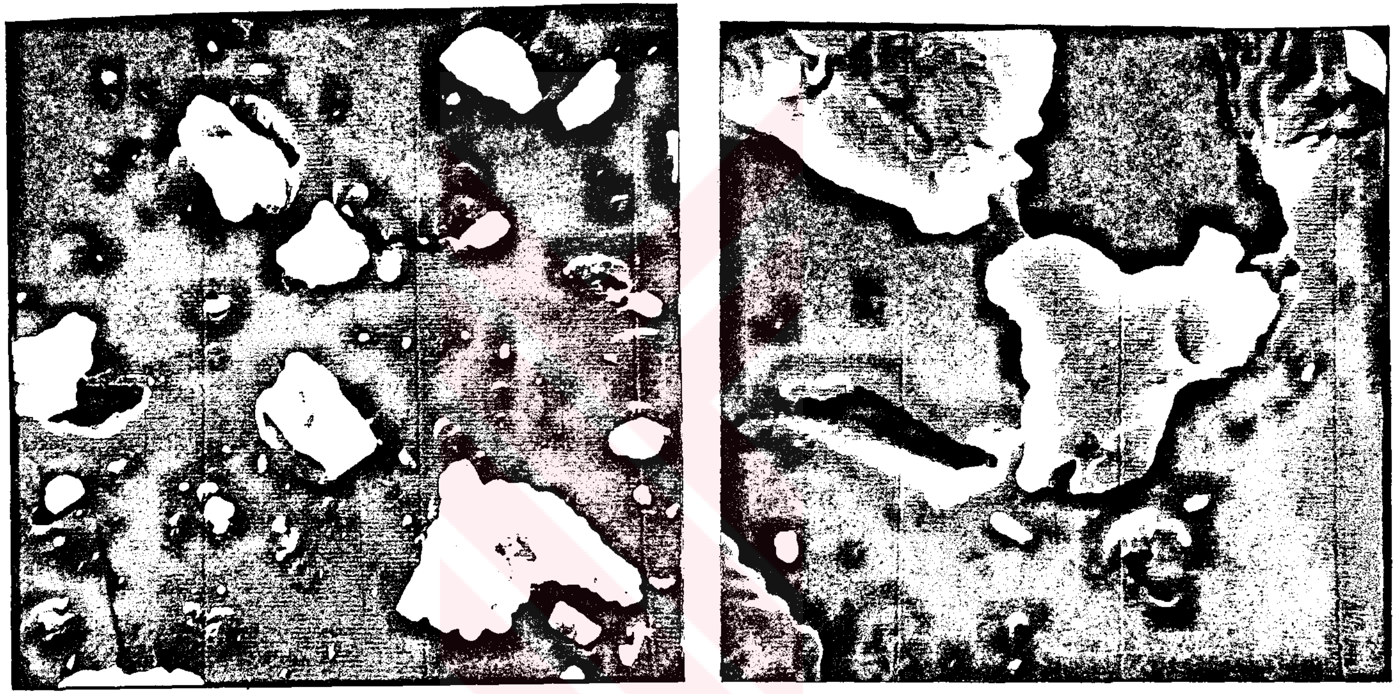
Figure.36. % Elongation vs. parts carbon black (solution casting data are also included) I=pps coated, II=uncoated, III=ppb coated



X 4000

X 8000

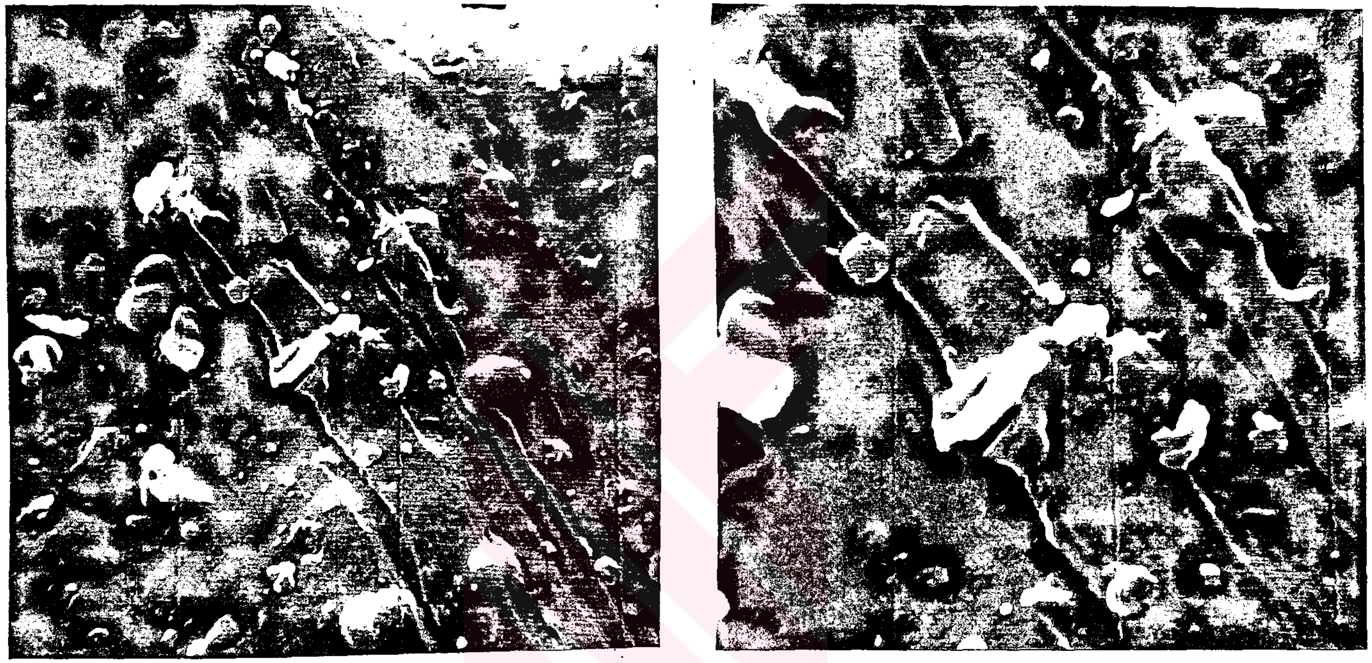
Figure.37. SEM photographs of uncoated bauxite filled SBR 1502 (fracture surfaces)



X 4000

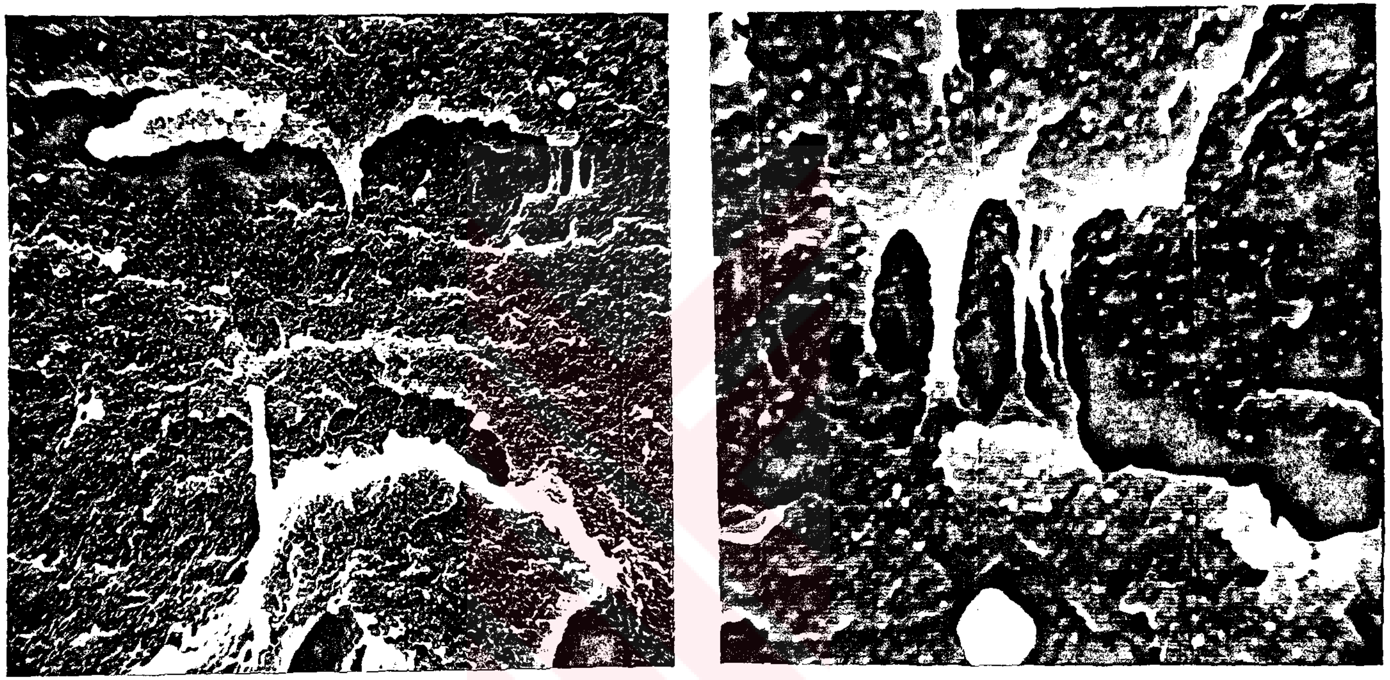
X 8000

Figure.38. SEM photographs of pps coated bauxite filled SBR 1502
(fracture surfaces)



X 4000 X 8000

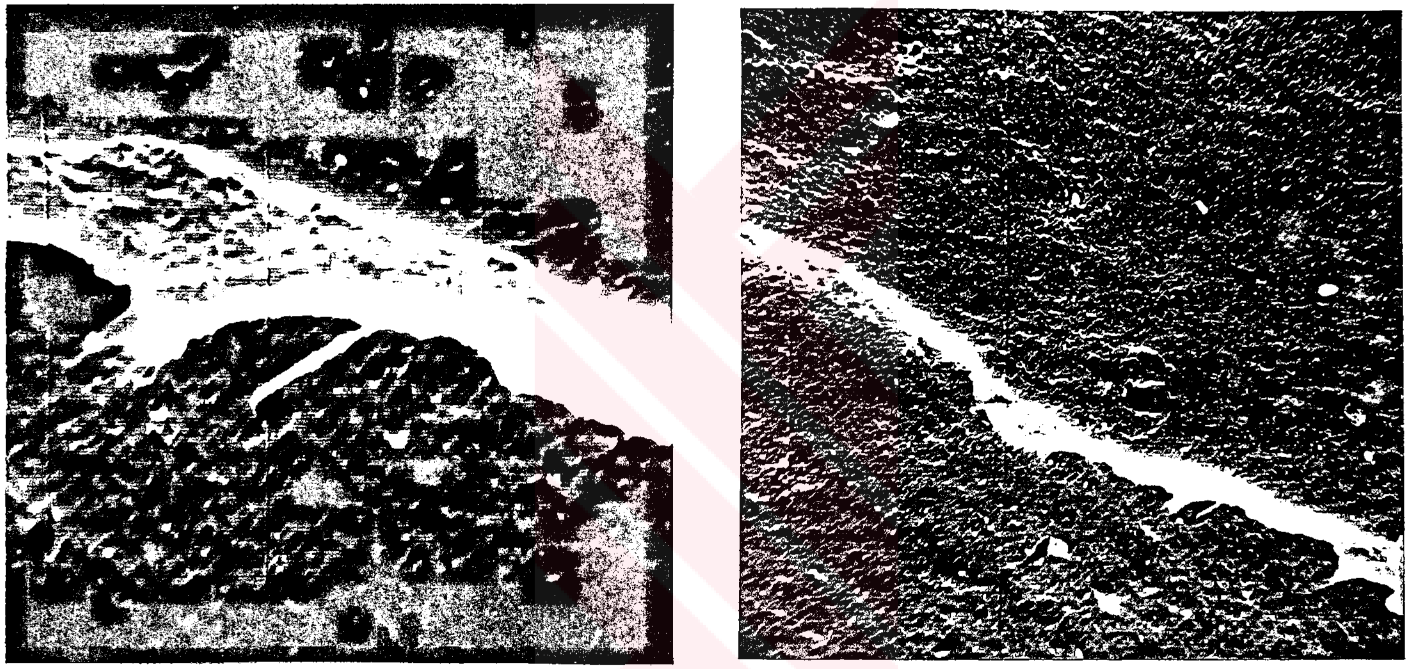
Figure.39. SEM photographs of ppb coated bauxite filled SBR 1502 (fracture surfaces)



X 1600

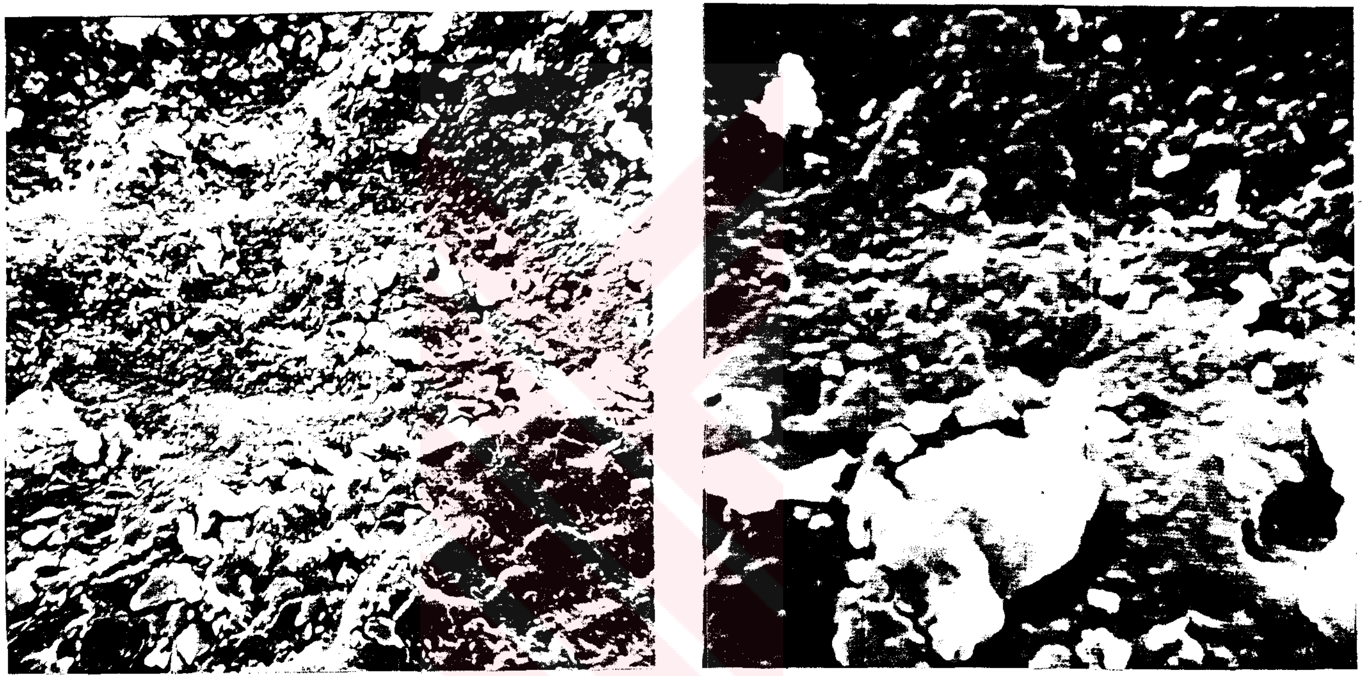
X 8000

Figure.40. SEM photographs of pps coated carbon black filled SBR 1502 (fracture surfaces)



X 1600 X 8000

Figure.41. SEM photographs of ppb coated carbon black filled SBR 1502 (fracture surfaces)



X 1600

X 8000

Figure.42. SEM photographs of uncoated carbon black filled SBR 1502 (fracture surfaces) polymer.

For the carbon black filled samples the adhesion phenomenon is very clear from figures 40 and 41 which belong to pps and ppb coated carbon black used samples respectively. From Figure 42 it is clear that when the selectivity of the carbon black has not been changed a very different surface pattern was obtained.

After this powerful support of electron microscope photographs a mathematical regression analysis of the experimental data was tried to be realized.For this purpose a computer program called "EUREKA" was used [47].

For the mathematical model the following assumptions were done :

1- There are three parameters effecting our system. These are cure kinetics, surface area and selectivity.

2- Among them,the cure kinetics have negligible effect for our specific system.

3- Selectivity is directly related to the percent of the corresponding component of the polymeric matrix, for this reason 0.25 (approximate styrene % of SBR) or 0.75 (approximate

% butadiene of SBR) numbers should be included in the proposed equation as constants.

4- Surface area effects should be represented in the equations as % decreases or increases.

5- Equations should be based on reference that is the uncoated filler used samples.

6- Solubility parameter of the polystyrene and polybutadiene should be included in the equations.

7- All selectivity effects should be assumed to increase the tensile strength of the samples with respect to the references.

8- All surface area decreases due to the coatings should be assumed to decrease the tensile strength of the samples with respect to the references.

9- All pps coatings should be assumed as to decrease the hardness of the samples with respect to the references.

10- All ppb coatings should be assumed as to increase the hardness of the samples with respect to the references.

11- Surface area differences of the fillers should be compensated by normalization in the equations and numbers seen in the equations have the following meanings:

17.6 = solubility parameter of polystyrene and polybutadiene ( $J/cm^3)^{1/2}$

0.25 = styrene content (%) of SBR

0.75 = butadiene content (%) of SBR

4.5 = surface area change (%) due to pps coating on bauxite

40.9 = surface area change (%) due to ppb coating on bauxite

7.6 = surface area change (%) due to ppb coating on carbon black

17.4 = ratio of surface area of carbon black to that of bauxite.

* surface area change (%) due to pps coating on carbon black was assumed as 0.0 %.

It is known from literature that there are several attempts to findout an equation by which the desired mechanical properties of the elastomers can be predicted [48-49]. After those equations were investigated the above assumptions were done and by those assumptions following equations were suggested :

TENSILE STRENGTH OF PPS COATED BAUXITE USED SAMPLES

$$TS = TS_o + 17.6^A * B * 0.25^E * F - 4.5^C * D$$

$$3.39 = 2.85 + 17.6^A * B * 0.25^E * F - 4.5^C * D$$

TENSILE STRENGTH OF PPB COATED BAUXITE USED SAMPLES

$$TS = TS_o + 17.6^A * B * 0.75^E * F - 40.9^C * D$$

$$2.74 = 2.85 + 17.6^A * B * 0.75^E * F - 40.9^C * D$$

TENSILE STRENGTH OF PPS COATED CARBON BLACK USED SAMPLES

$$TS = TS_o + 17.6^A * B * 0.25^E * F - 0.0^C * D * 17.4$$

$$27.73 = 25.98 + 17.6^A * B * 0.25^E * F$$

TENSILE STRENGTH OF PPB COATED CARBON BLACK USED SAMPLES

$$TS = TS_o + 17.6^A * B * 0.75^E * F - 7.6^C * D * 17.4$$

$$17.68 = 25.98 + 17.6^A * B * 0.75^E * F - 7.6^C * D * 17.4$$

When these equations were solved with "EUREKA", the constants got the following values:

A= - 0.41758778

B= 1.0490144

C= 0.016762099

D= 0.48371712

E= - 1.1126022

F= 0.93475048

If the equations are evaluated with these constants following results are obtained:

| VALUES | FORMULAS | DIFFERENCE |
|---|---|---|
| 3.39 = | 3.7381985 | -0.34819850 |
| 2.74 = | 2.7429677 | -0.0029676679 |
| 27.73 = | 27.3642660 | .36573412 |
| 17.68 = | 17.6800000 | 00000000 |

If the same procedure is repeated for hardness equations:

HARDNESS OF THE PPS COATED BAUXITE USED SAMPLES

$$\text{HARDNESS} = \text{HARDNESS}_o - 17.6^a * 0.25^b * c - 4.5^d * e$$

$$49 = 50.5 - 17.6^a * 0.25^b * c - 4.5^d * e$$

HARDNESS OF THE PPB COATED BAUXITE USED SAMPLES

$$\text{HARDNESS} = \text{HARDNESS}_o + 17.6^a * 0.75^b * c - 40.9^d * e$$

$$56 = 50.5 + 17.6^a * 0.75^b * c - 40.9^d * e$$

## HARDNESS OF THE PPS COATED CARBON BLACK USED SAMPLES

$$\mathrm{HARDNESS} = \mathrm{HARDNESS}_o - 17.6^a * 0.25^b * c - 0.0^d * e$$

$$64 = 66 - 17.6^a * 0.25^b * c$$

## HARDNESS OF THE PPB COATED CARBON BLACK USED SAMPLES

$$\mathrm{HARDNESS} = \mathrm{HARDNESS}_o + 17.6^a * 0.75^b * c - 7.6^d * e * 17.4$$

$$67 = 66 + 17.6^a * 0.75^b * c - 7.6^d * e * 17.4$$

When these equations were solved with "EUREKA", the constants got the following values:

a= 0.71535859

b= 1.0158254

c= 1.0510652

d= 0.47515128

e= 0.11192992

If the equations are evaluated with these constants following results are obtained:

| VALUES | FORMULAS | DIFFERENCE |
|---|---|---|
| 49 = | 48.2712710 | .72872885 |
| 56 = | 55.9524600 | .047539555 |
| 64 = | 64.0000000 | 00000000 |
| 67 = | 67.0000000 | 00000000 |

To see whether the same trends of tensile strength and hardness are observable or not same experiments were repeated with a new polymer that is SBR 1516. As it was mentioned in the materials part, SBR 1516 contains 40 % styrene. It should be mentioned here that the same conditions for ppb coating of carbon black couldn`t be reached and it was observed that polymer seen at the reactor surface is very low when compared with the previous ppb coatings. Probably the surface area of this new carbon black is not low as the old one is (it was 106.2 $m^2/g$), although it should be lower than 114.9 $m^2/g$ .

When these new samples were tested for their mechanical properties it was observed that all trends are preserved. For example the hardness of the original sample is 70-71 Shore A, while the pps and ppb coated samples are 69-70 and 71-72 Shore A respectively. On the other hand the tensile strength of the original sample was 12.42 MPa. This value has been increased to 13.70 MPa due to the pps coatings while it has beeen decreased to 10.55 MPa due to ppb coatings. There are three more observations of these new samples.First is that although the recipe and processing conditions are the same there is a large difference between the strengths of the samples prepared from different SBR polymers. This is clearly because of the styrene content, molecular weight, molecular weight distribution differences of two rubbers. The second observation is that the decrease of the tensile strength due to the ppb coating is not as in the case of SBR 1502. But the observation of small amount of polymer at the reactor surface during plasma polymerization strongly suggests that the surface area decrease in this case is so small than the previous coatings. So the structural reinforcing effect of carbon black should not change sharply. This proposition was supported experimentally where although the same trends are preserved the decrease in tensile strength of the ppb coated sample is small . The third observation is that these samples are harder than the ones where the matrix was SBR 1502. The reason for this fact is simply the increased styrene content of SBR 1516. The results of the tests done for SBR 1516 are given in Table 9 and Figures 43-48.

Later on the same procedure for both coatings and mechanical properties were repeated for a new filler that is Sill-cell 150.The detailed information of the Sill-cell is given in the material part.But it should be repeated here once more that the particle size of the Sill-cell 150 is very large (5 000-150 000 nm) and it is mainly $SiO_2$. The surface areas of the Sill-cells could not be measured accurately since the values were out of the sensitivity levels of the instruments used. But it can be said that the values are changing in between 1-2 $m^2/g$. The hardness` of the uncoated, pps coated, and ppb coated Sill-cells filled samples were 57.5, 55.5, and 59.5 Shore A

| SAMPLE | HARDNESS<br>SHORE A | Tg<br>C | Tan<br>d | TENSILE STRENGTH<br>MPa | ELONGATION<br>% |
|---|---|---|---|---|---|
| UNFILLED | 37-40 | -0.3 | 1.47 | - | - |
| BAUXITE | 50.5 | 4.6 | 1.65 | - | - |
| PPS COATED BAUXITE | 50-50.5 | 4.5 | 1.65 | - | - |
| CARBON BLACK | 70.5 | 10.2 | 0.75 | 12.42 | 587 |
| PPS COATED CARBON BLACK | 69-70 | 10.1 | 0.75 | 13.70 | 673 |
| PPB COATED CARBON BLACK | 71-72 | 7.5 | 0.73 | 10.55 | 662 |

Table.9. Complete data of SBR 1516 system

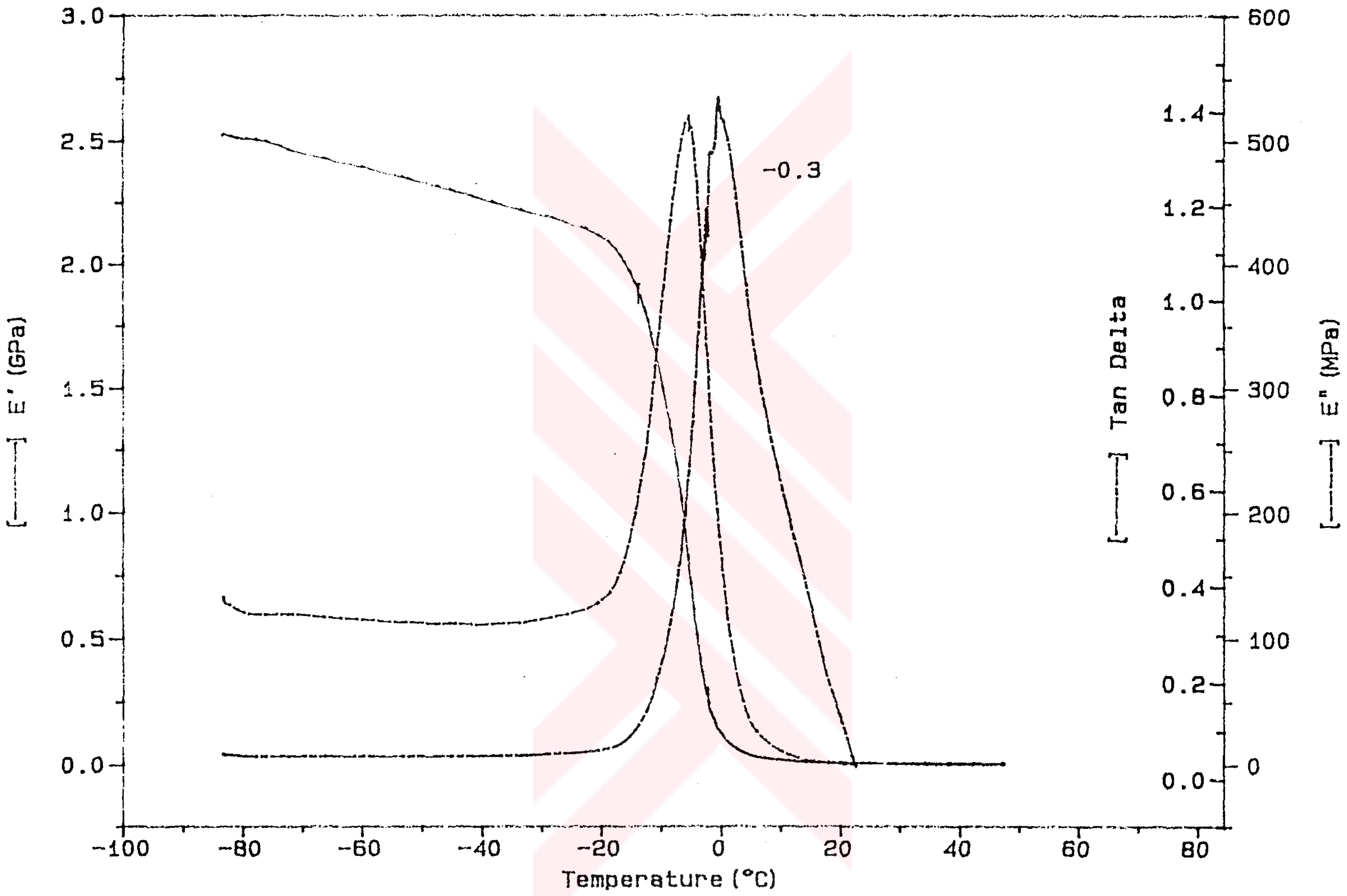


Figure.43. DMA of unfilled SBR 1516

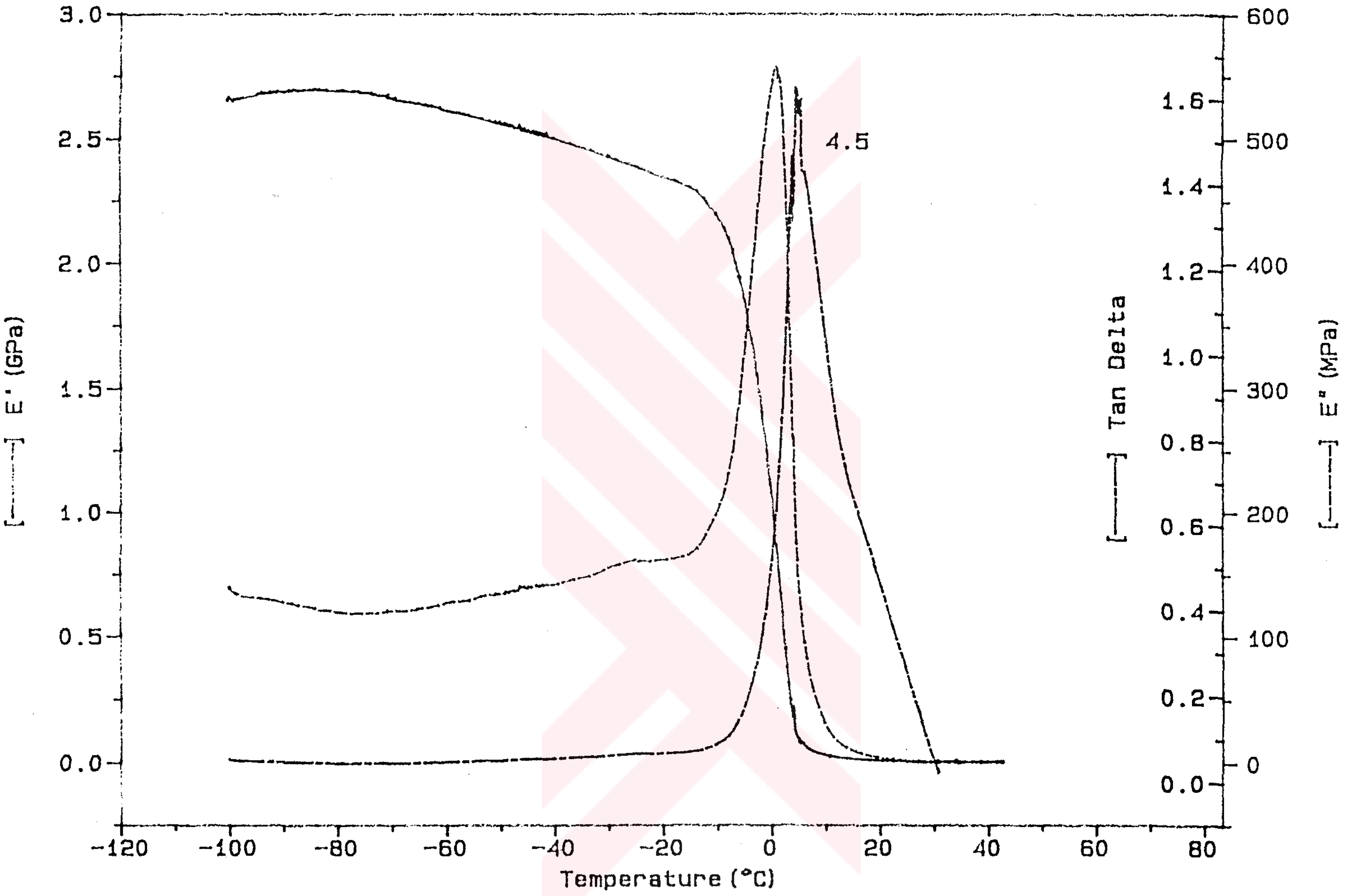


Figure.44. DMA of uncoated bauxite filled SBR 1516

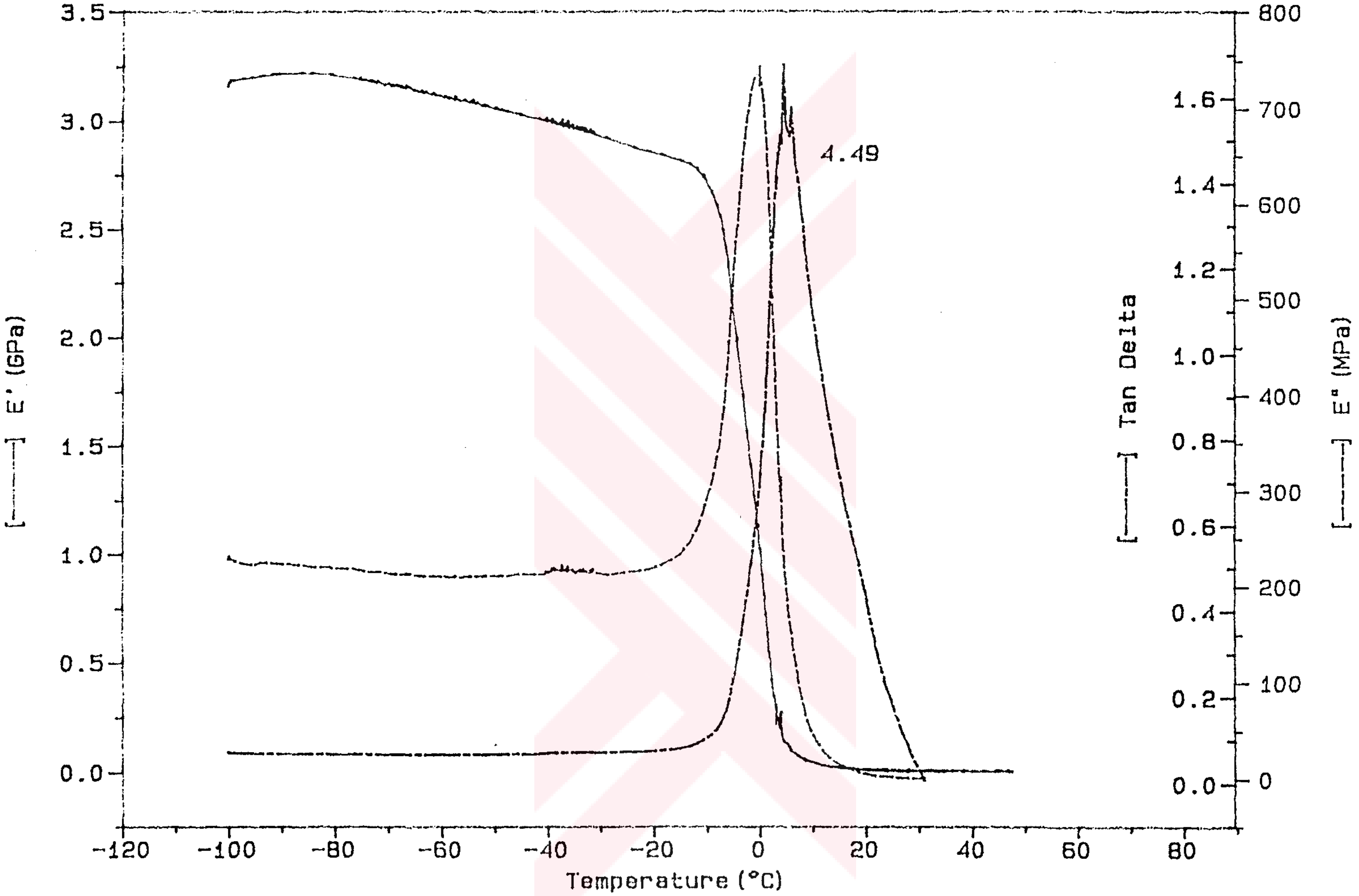


Figure.45. DMA of pps coated bauxite filled SBR 1516

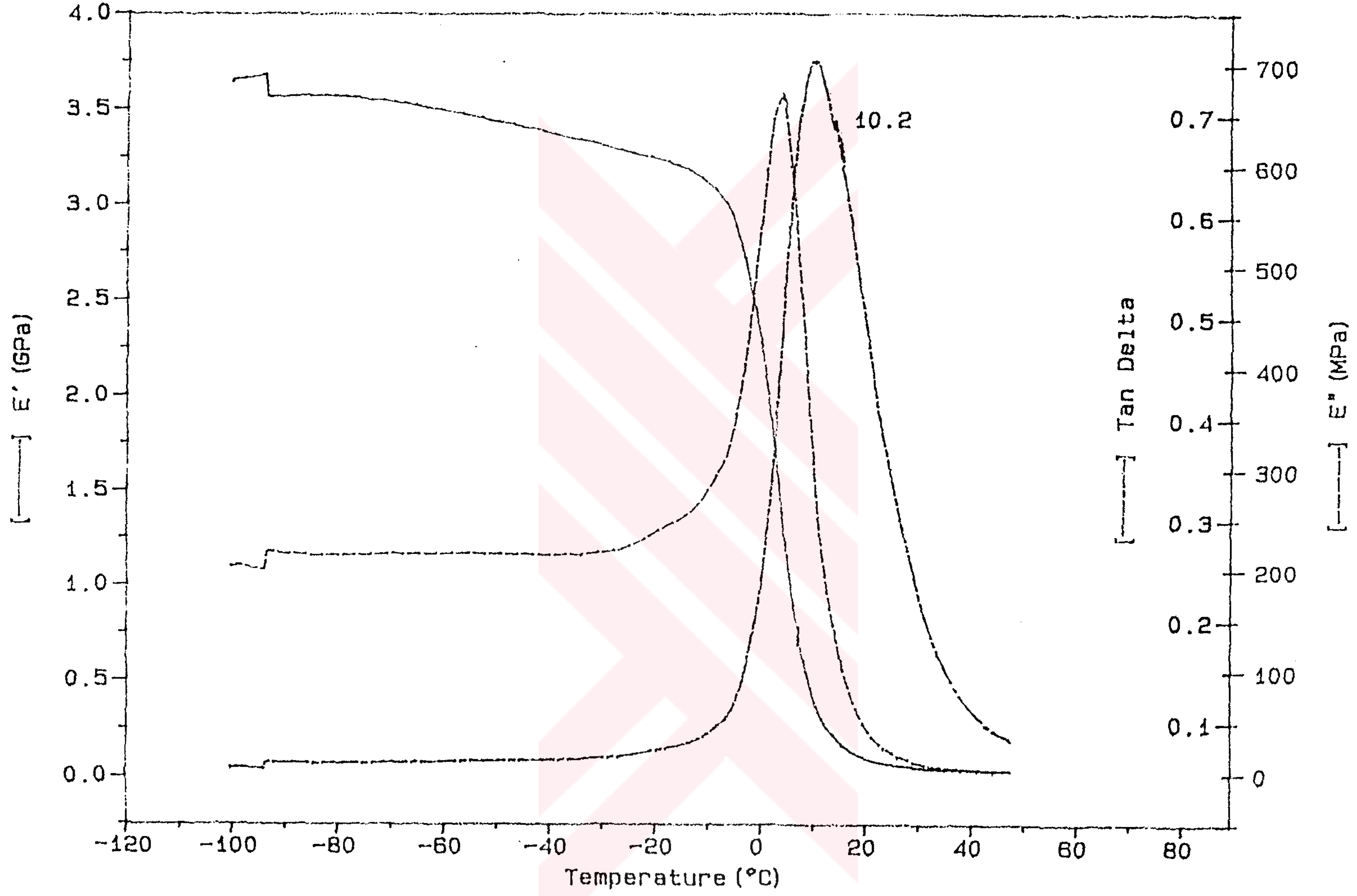


Figure.46. DMA of uncoated carbon black filled SBR 1516

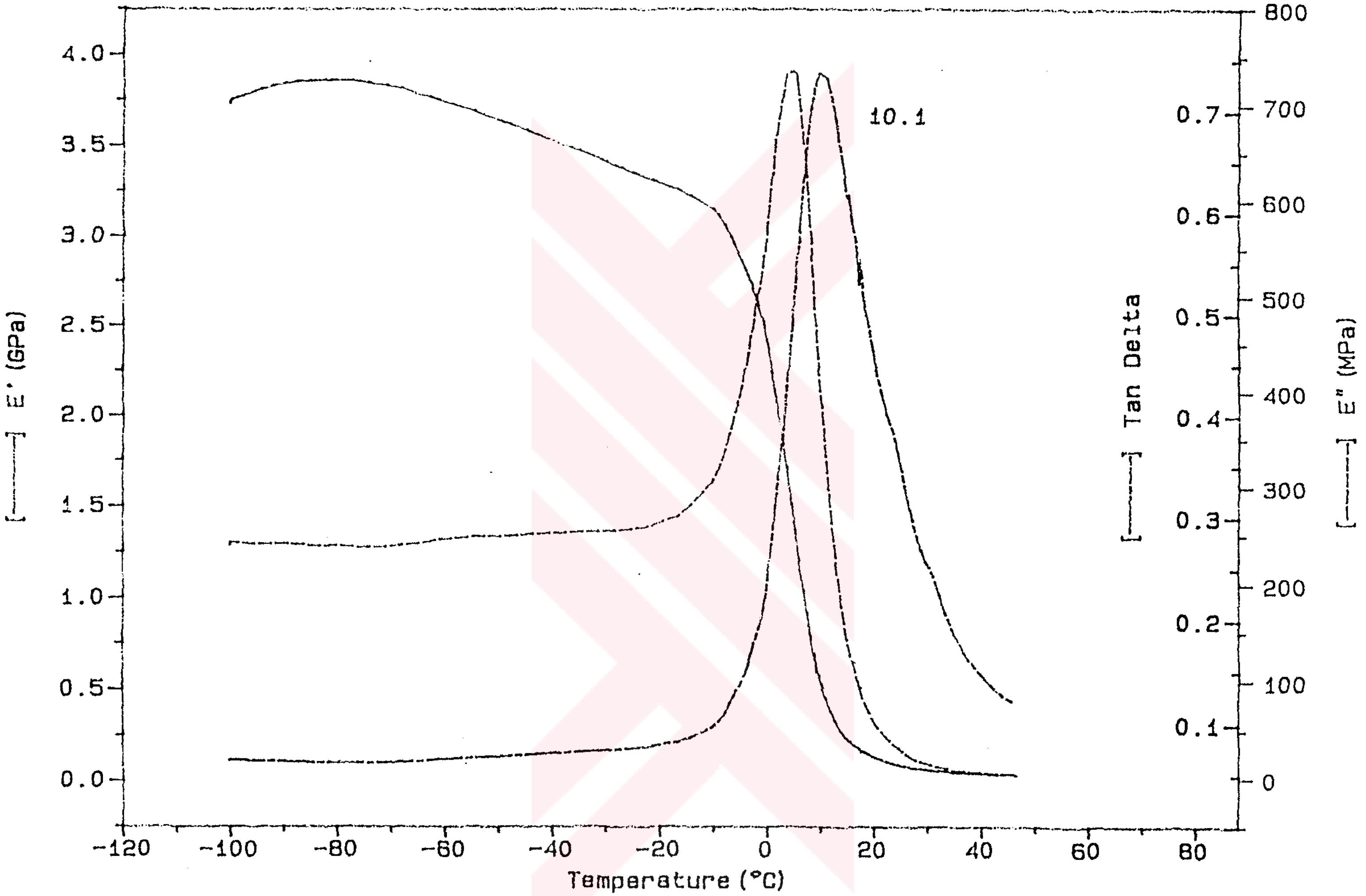


Figure.47. DMA of pps coated carbon black filled SBR 1516

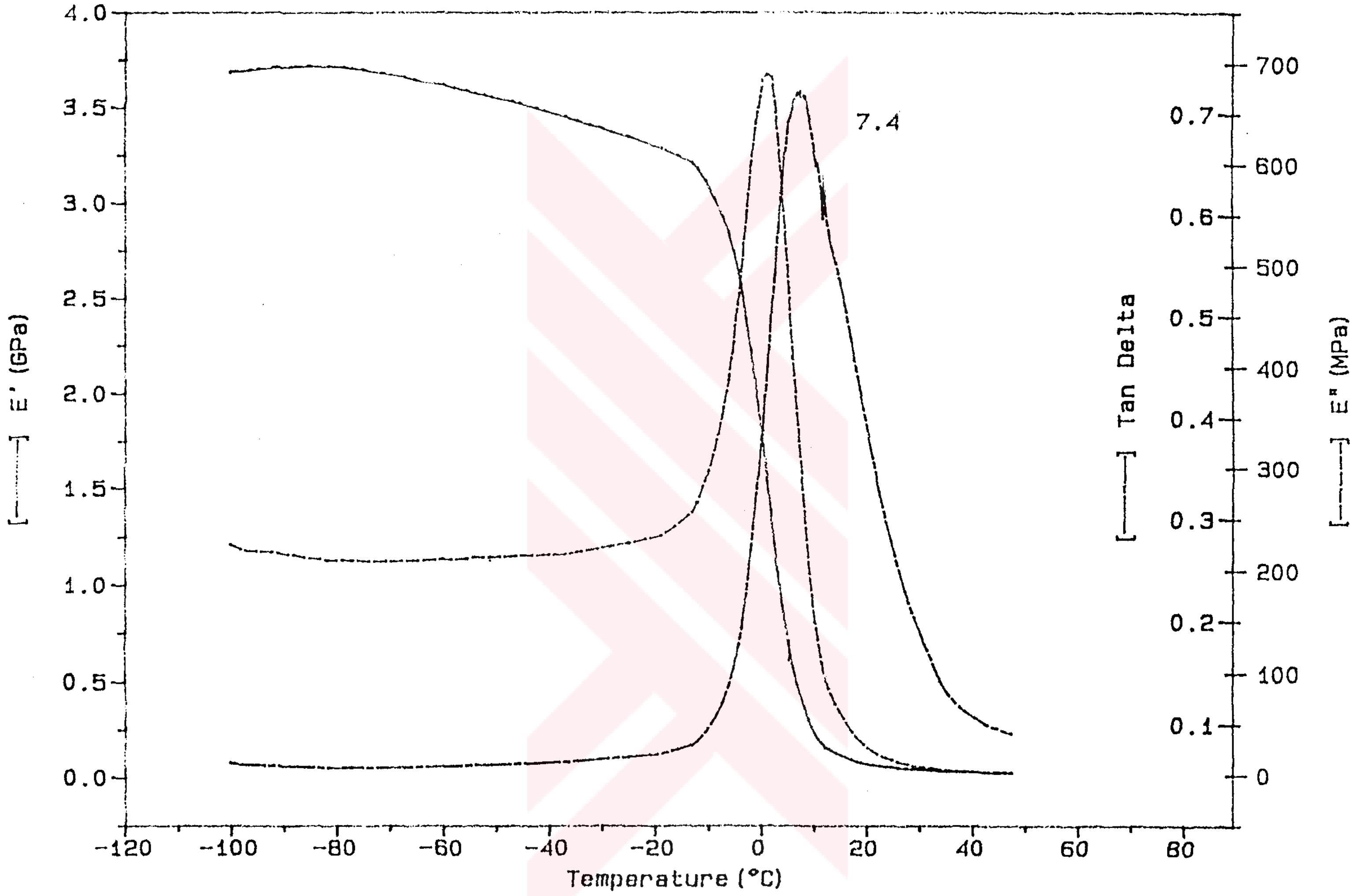


Figure.48. DMA of ppb coated carbon black filled SBR 1516

respectively. So the trends of softening due to pps coating and hardening due to ppb coating were preserved. The tensile strength and % elongation were very similar to each other and a meaningful $T_g$ shifts could not be observed. There were two more original Sill-cells which are silane treated and silicon treated. Similar observations of the mechanical properties were valid for these samples too except the silicon treated one had a $T_g$ of - 30.5 $^{o}$C. This sudden decrease of $T_g$ was noted for silicon treatment and to see a similarity some Sill-cell was coated with polyhexamethyldisiloxane with again pasma polymerization for 15 minutes at 16 watt of power. The $T_g$ of this sample was-20.54 $^{o}$C.So more or less a similarity was observed. The results of the Sill-cell experiments were listed in Table 10 and Figures 49-61.

On the other hand similar procedures were repeated for a new polymer which was styrene-butadiene-styrene (SBS) block copolymer by using carbon black and bauxite as fillers.

In the first series of experiments 35 parts uncoated, pps coated and ppb coated bauxite were loaded to SBS without adding any sulfur. It was observed that the tensile strength of uncoated and pps coated carbon black filled samples have the same values which is 22 MPa. The ppb coated carbon black filled sample had a tensile strength of 19 MPa. The % elongation values of all these samples were around 1450. The hardness of these

| SAMPLE | PARTICLE SIZE nm | SURFACE AREA M**2/gm | HARDNESS SHORE A | Tg C | Tan d | TENSILE STRENGTH MPa | ELONGATION % |
|---|---|---|---|---|---|---|---|
| SILL CELL 150 | 5000-15000 | 1-2 | 57.5 | - 15.5 | 1.3 | 3.97∓0.33 | 417∓84 |
| PPS COATED SILL CELL 150 | - | 1-2 | 55.5 | - 21.1 | 1.3 | 3.44∓0.42 | 375∓43 |
| PPB COATED SILL CELL 150 | - | 1-2 | 59.5 | - 22 | 1.4 | 4.13∓0.22 | 486∓47 |
| SILL CELL 150H (SILANE) | - | 1-2 | 59.5 | - 14 | 1.3 | 4.30∓0.73 | 489∓114 |
| SILL CELL 150-23 (SILICONE) | - | 1-2 | 59.5 | - 30.5 | 1.3 | 3.94∓0.52 | 415∓31 |
| PPHMDS COATED SILL CELL 150 | - | 1-2 | 61.5 | - 20.5 | 1.2 | 3.96∓0.18 | 586∓15 |

Table.10. Complete data of Sill cell 150 filled SBR 1502 system

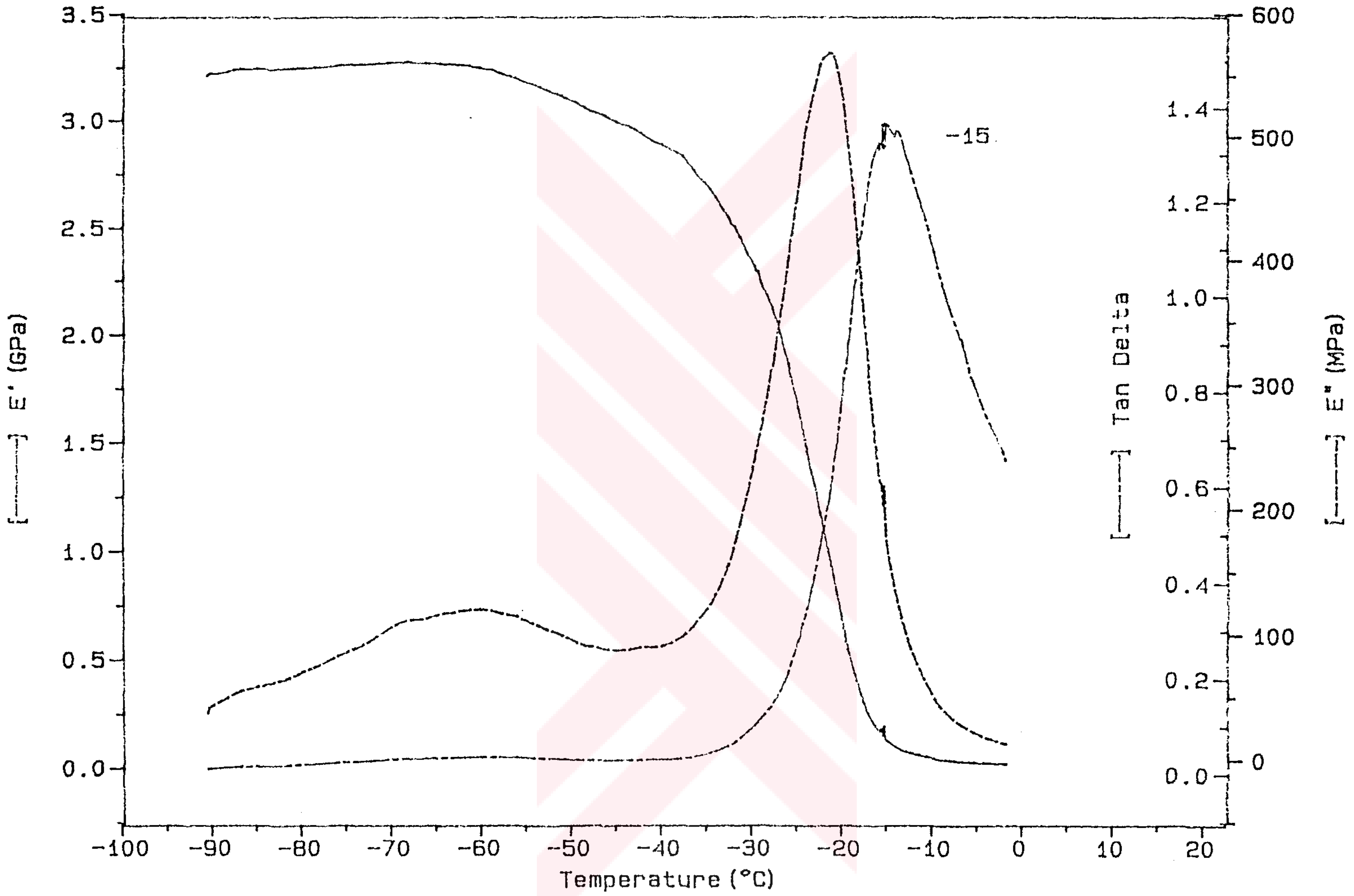


Figure.49. DMA of sill-cell 150 filled SBR 1502

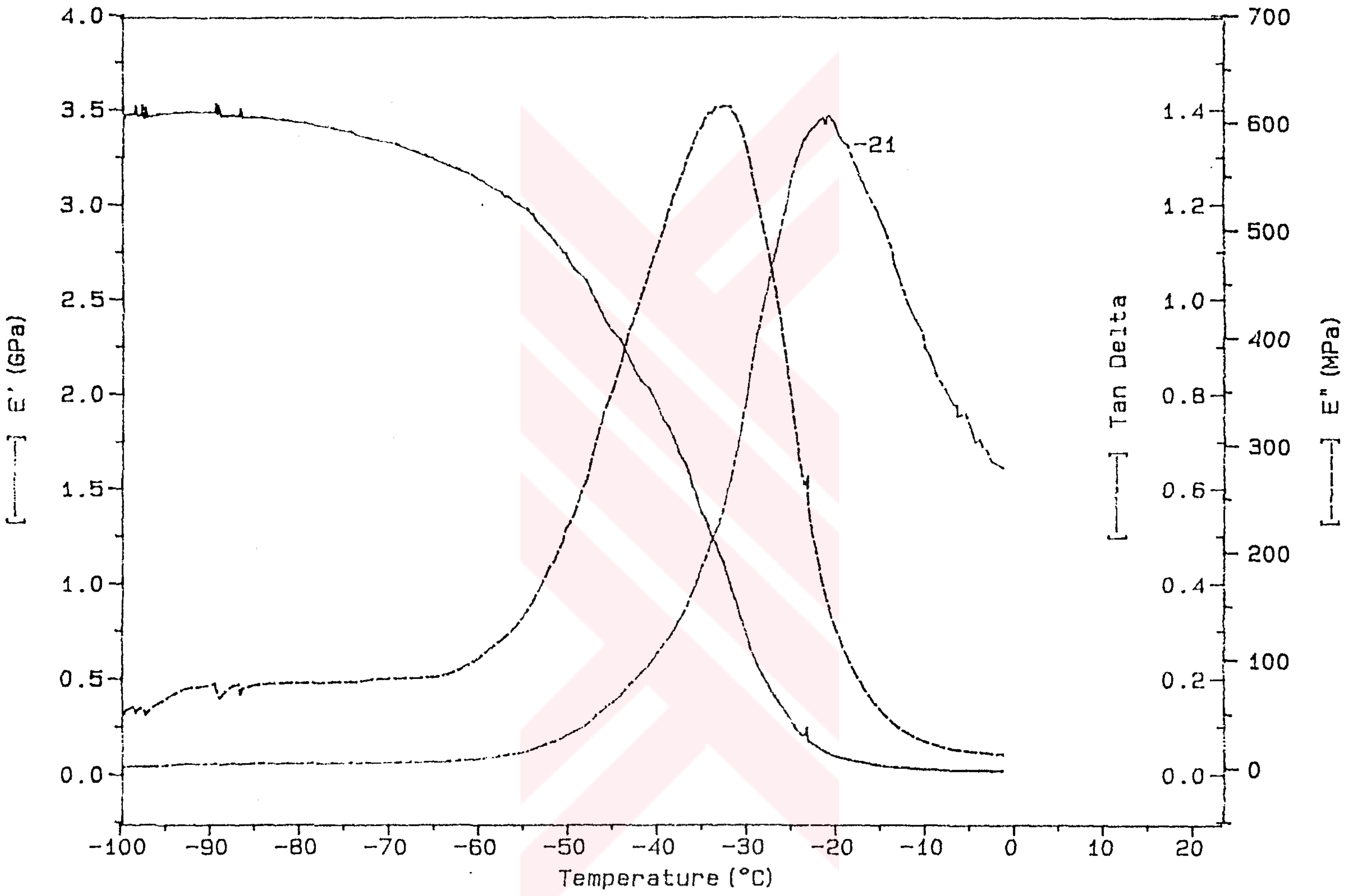


Figure.50. DMA of pps coated sill-cell 150 filled SBR 1502

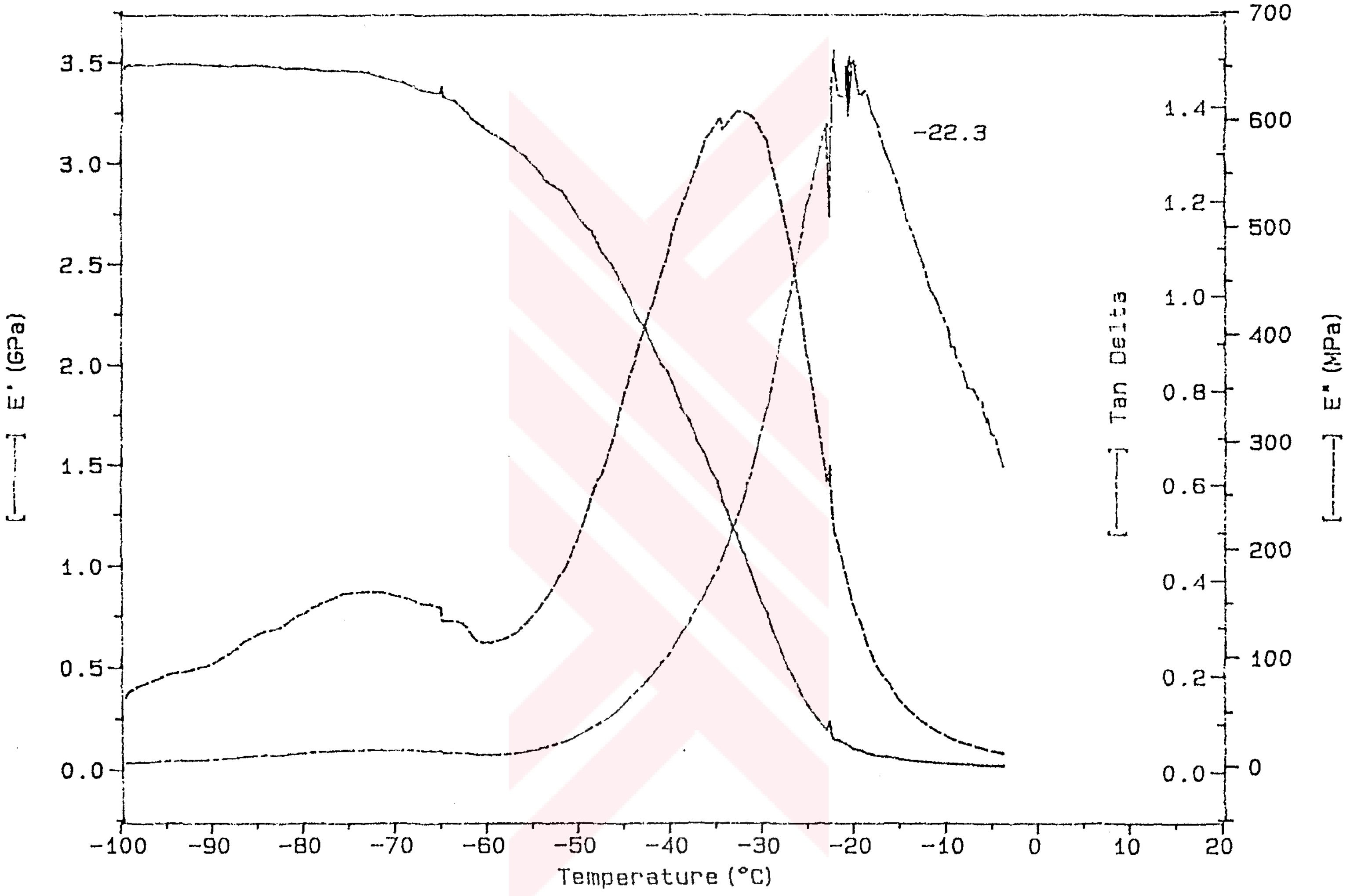


Figure.51. DMA of ppb coated sill-cell 150 filled SBR 1502

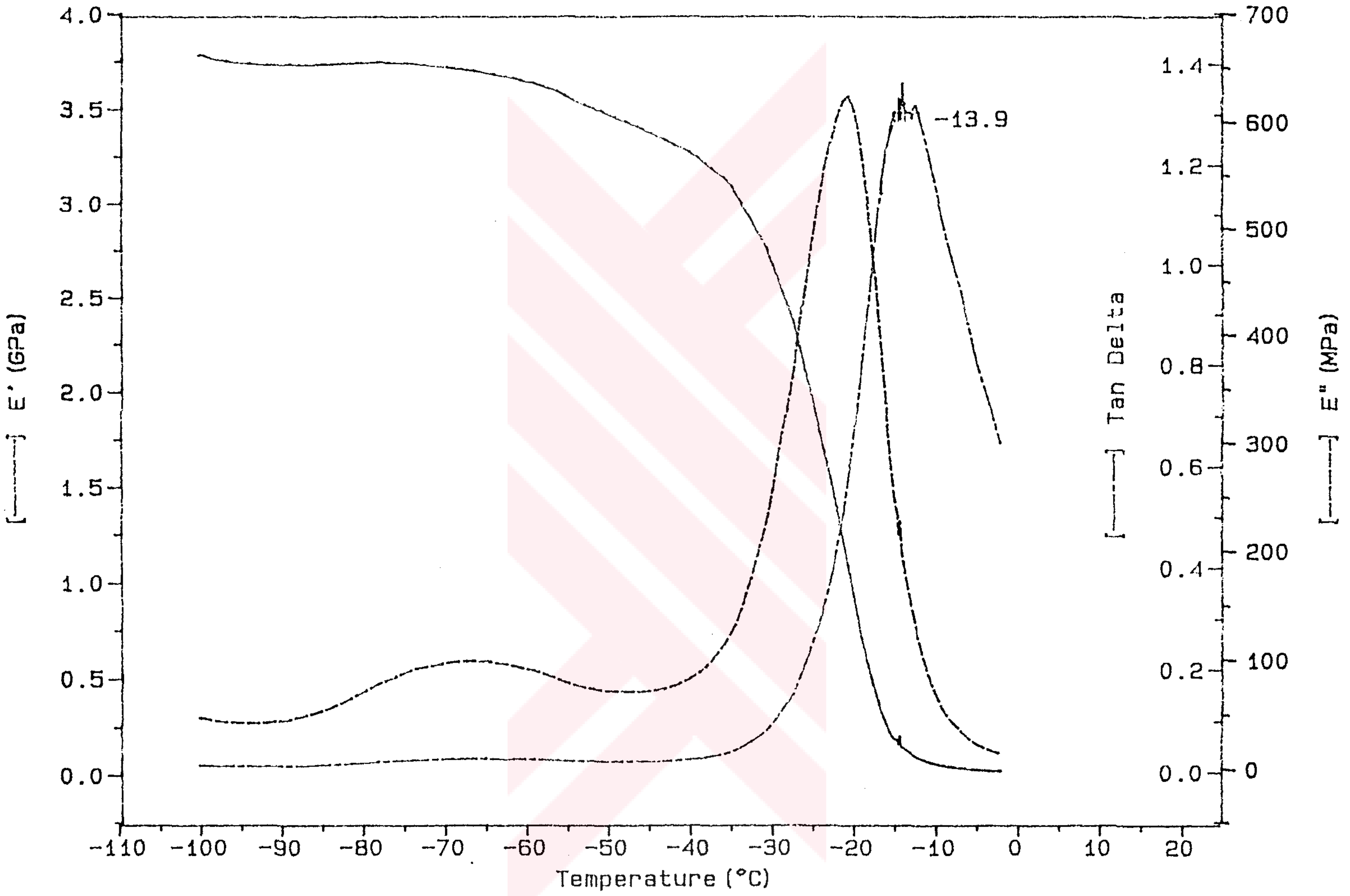


Figure.52. DMA of sill-cell 150-H (silane treated) filled SBR 1502

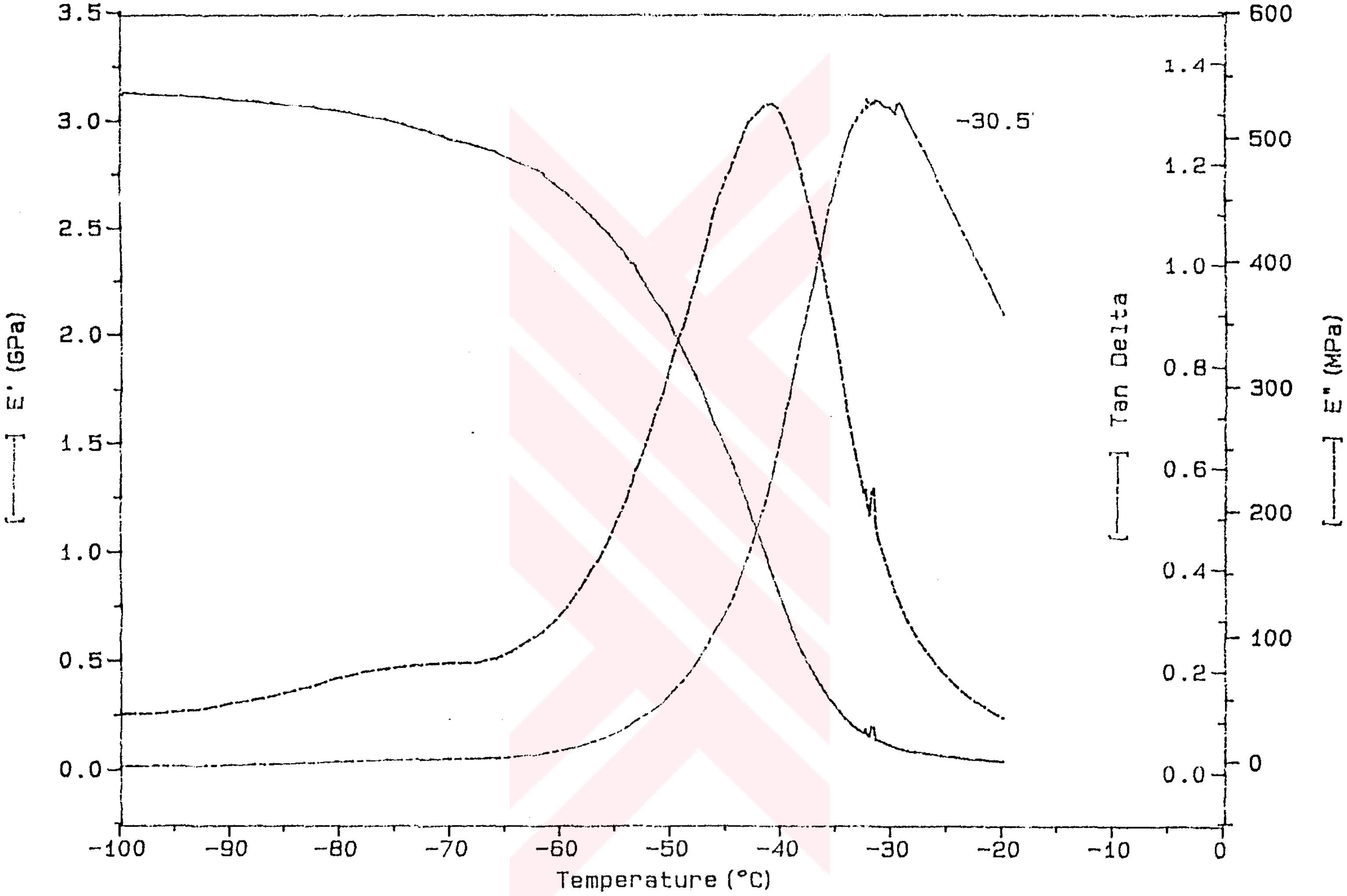


Figure.53. DMA of sill-cell 150-23(silicon treated) filled SBR 1502

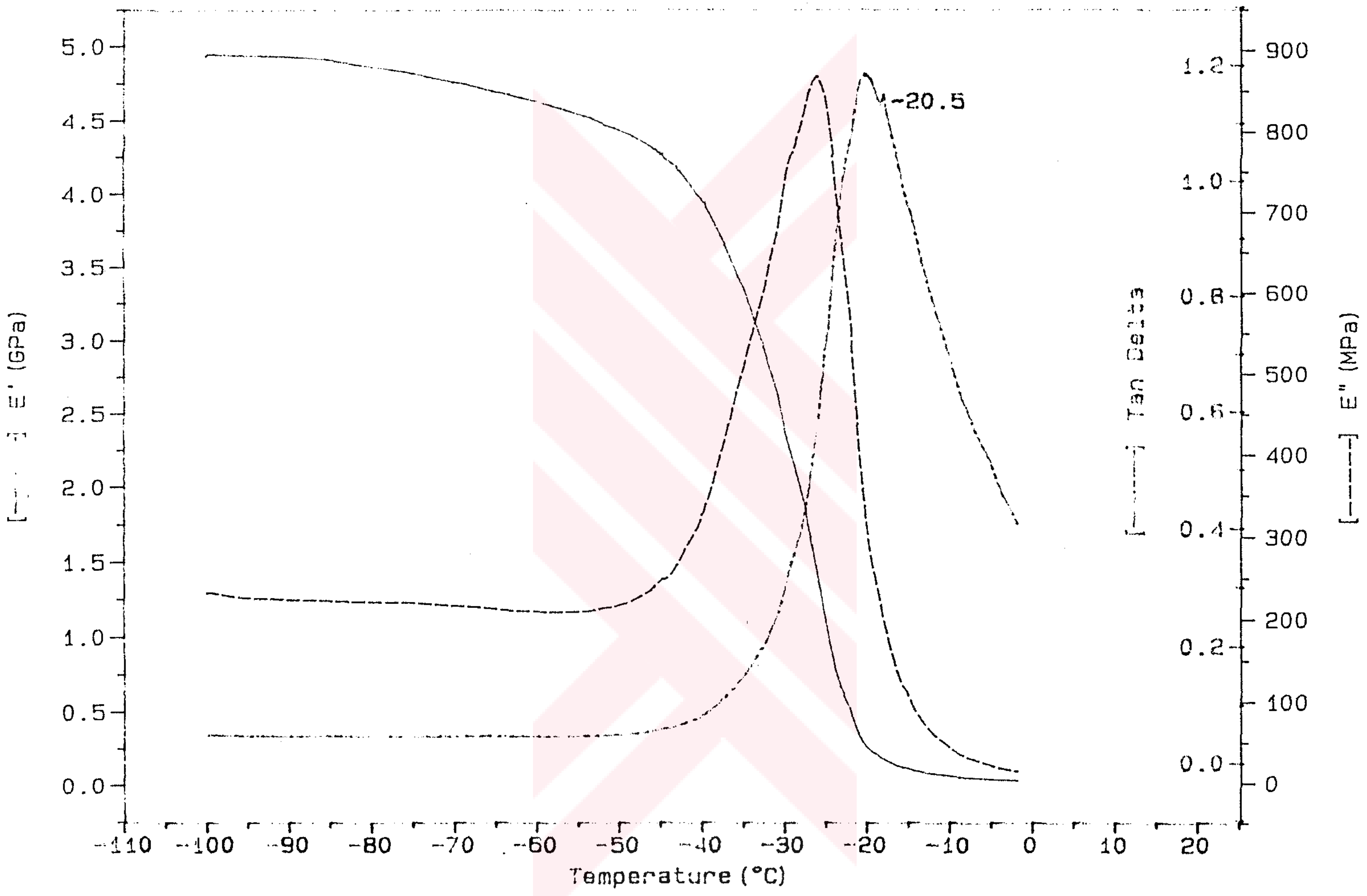


Figure.54. DMA of poly-hexamethyldisiloxane coated sill-cell 150 filled SBR 1502

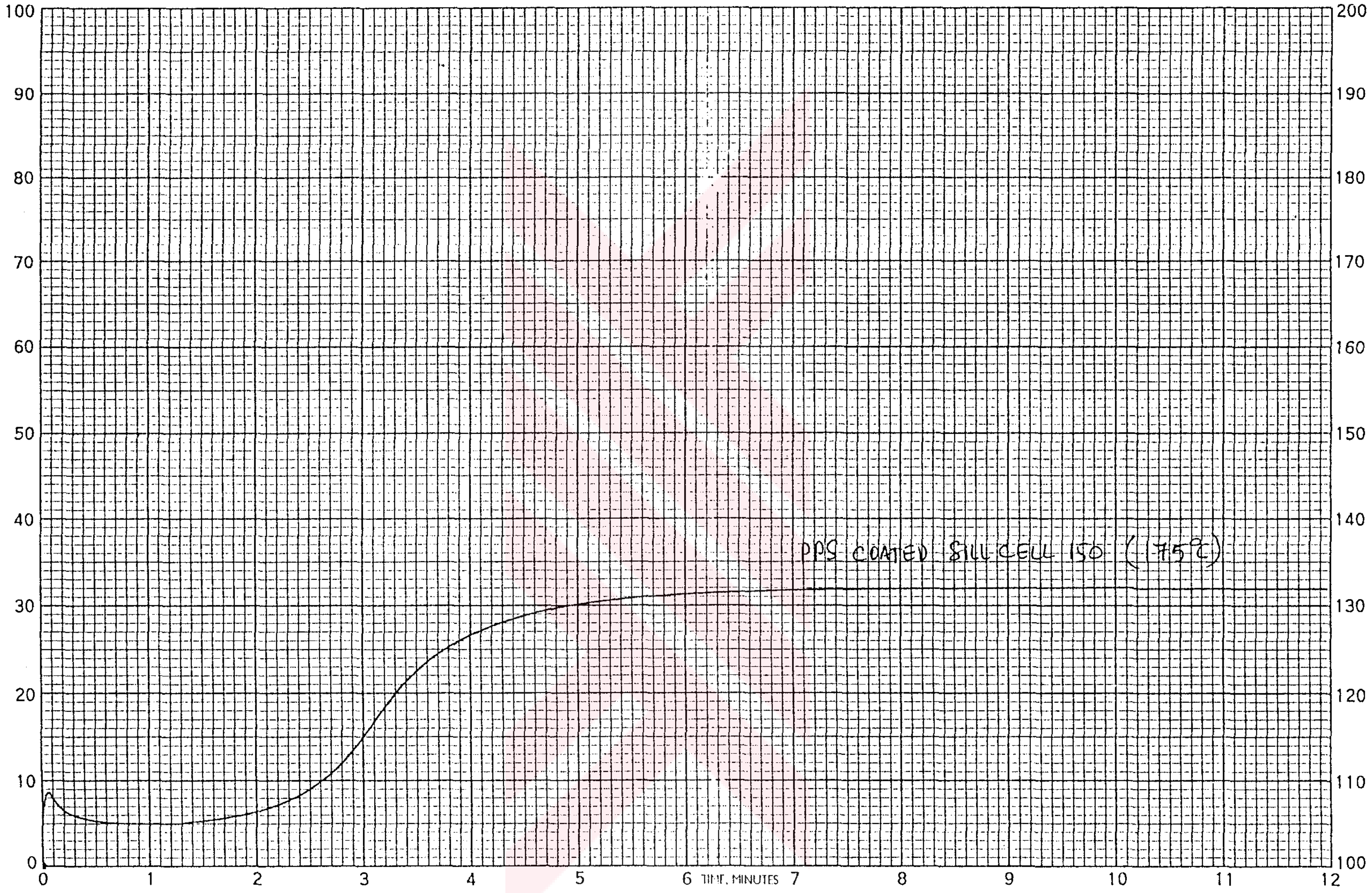


Figure.55. Rheometric attitude of pps coated sill-cell 150 filled final batch compound (175 °C)

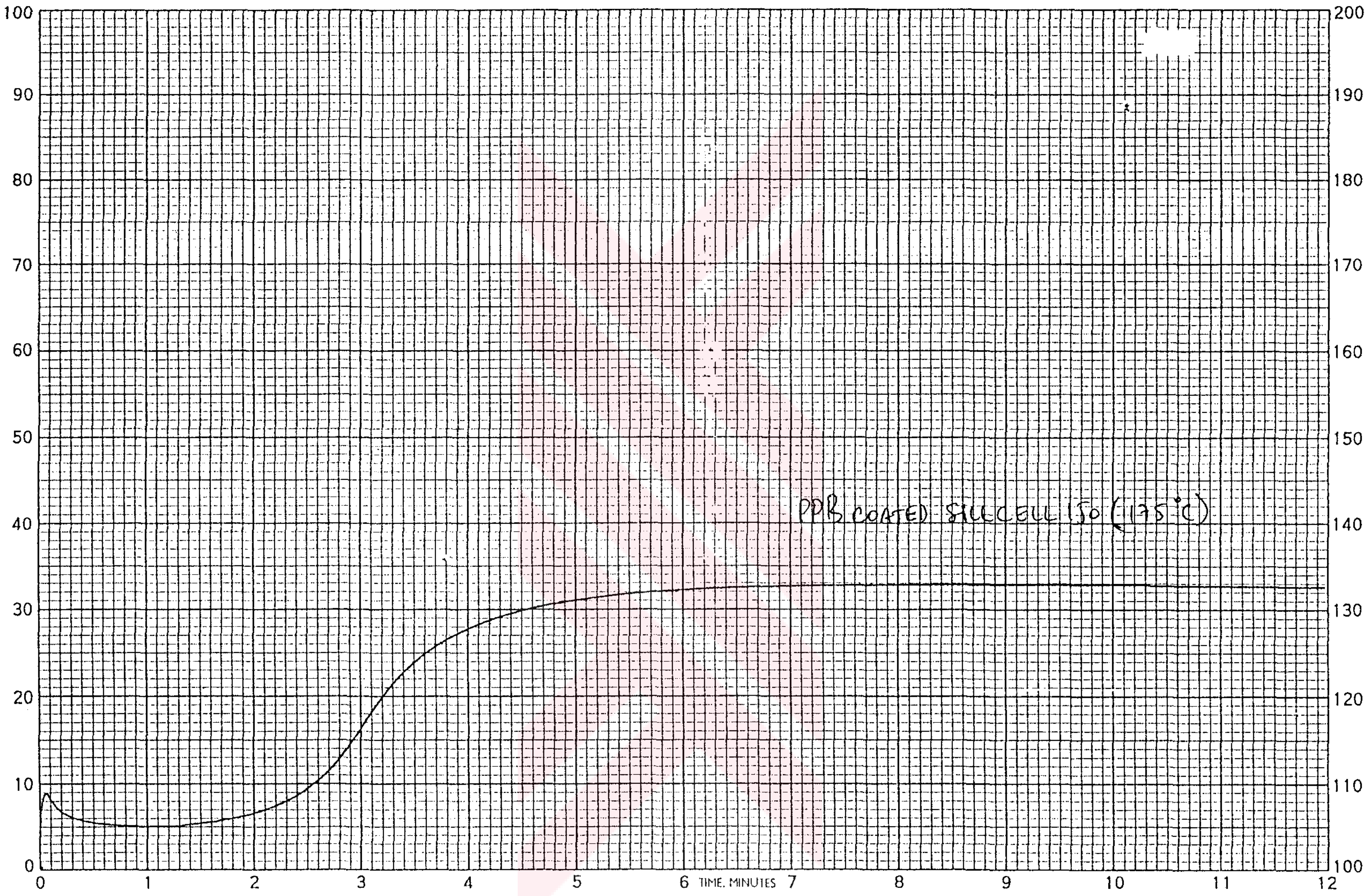
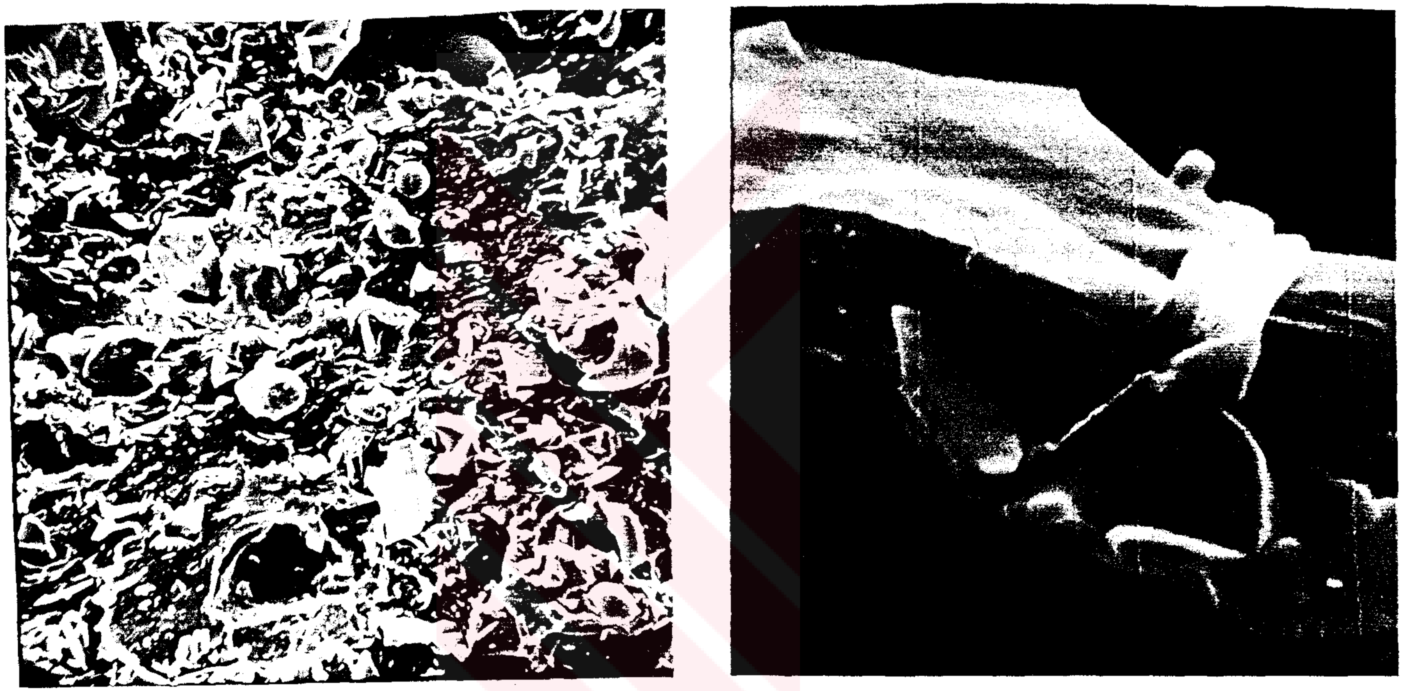


Figure.56. Rheometric attitude of ppb coated sill-cell 150 filled final batch compound (175 °C)



X 400 X 8000

Figure.57. SEM photographs of uncoated sill-cell 150 filled SBR 1502 (fracture surfaces)

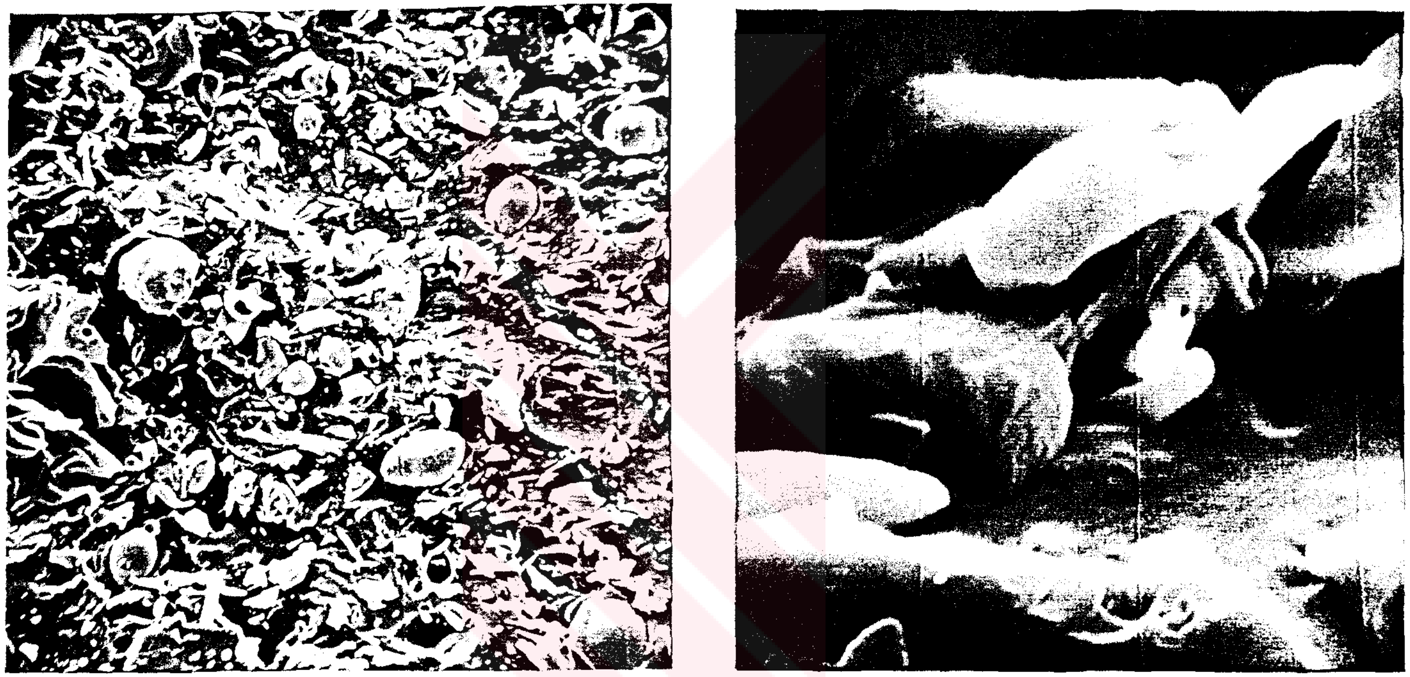
X 400

X 8000

Figure.58. SEM photographs of pps coated sill-cell 150 filled SBR 1502 (fracture surfaces)

X 400 X 8000

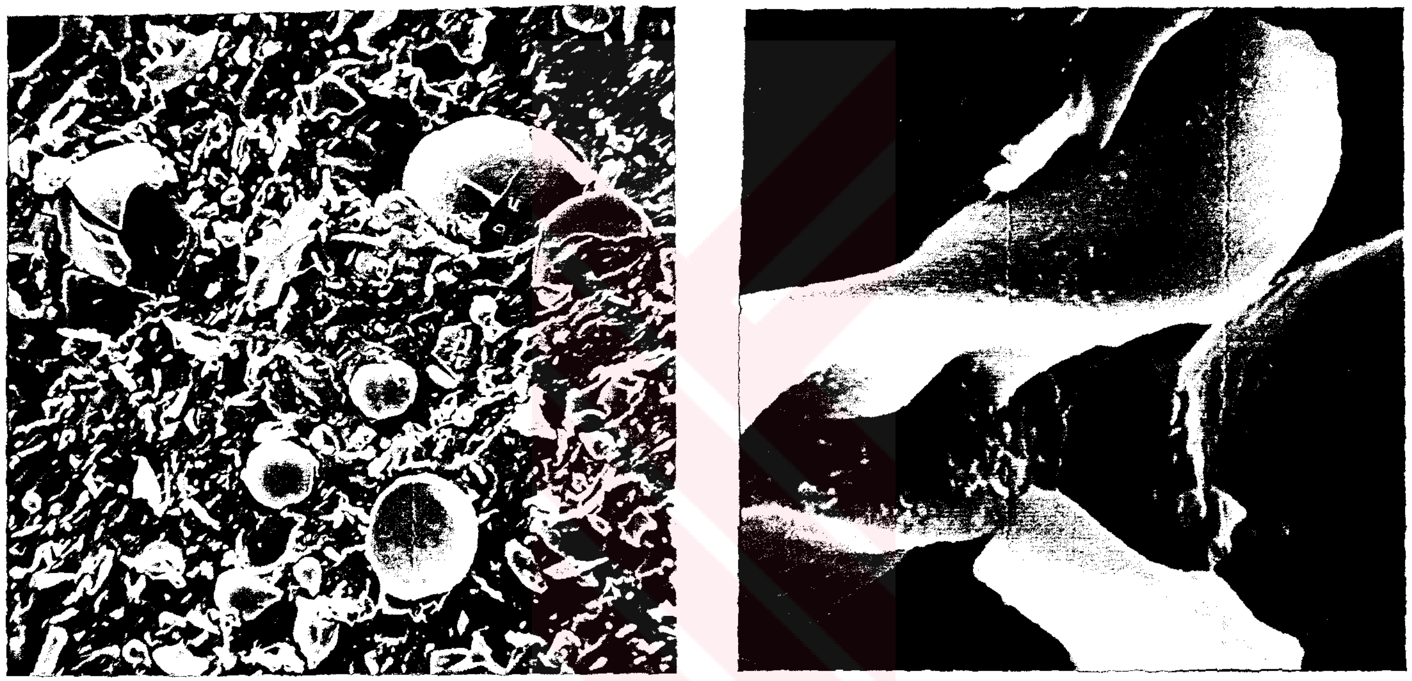
Figure.59. SEM photographs of ppb coated sill-cell 150 filled SBR 1502 (fracture surfaces)



X 400

X 8000

Figure.60. SEM photographs of sill-cell 150-H filled SBR 1502 (fracture surfaces)



X 400 X 8000

Figure.61. SEM photographs of sill-cell 150-23 filled SBR 1502 (fracture surfaces) samples were also the same and had a value of 80 Shore A. The tensile strength, % elongation and the hardness values of the pure SBS samples were 14 MPa, 900 %, and 77.5 Shore A respectively. Another important observation for these samples was the shape of the stress strain curves. For the uncoated and ppb coated samples the shape of those curves were the same. But the pps coated sample has shown a different behaviour by giving a yield point although it was absent for uncoated and ppb coated bauxite filled samples. On the other hand it was observed that mixing of SBS with such a loading of filler is very difficult. For this reason 5 parts of the uncoated, pps coated and ppb coated carbon blacks were tried to incorporate into the matrix without addition of sulfur again. The results for the tensile strength, % elongation, and hardness values were all same and 25 MPa, 1500 %, and 79 Shore A respectively. The shape of the stress strain curves were also same for these samples. This 5 parts loading experiments were repeated by using sulfur also and it was seen that tensile strength and % elongations have been decreased up to 8.5 MPa and 385 % elongation while the hardness values are same and 80 Shore A this time. It was also noted that the shape of the stress strain curves of the samples with and without sulfur are different from each other since the slope of the curve after yield point for sulfur used sample is considerably greater than that of the sulfurless system.

The effect of different mixing conditions was also tried to be seen roughly for these samples. For this purpose the sulfur containing system was mixed at a higher speed of the mixer rotor for a longer time period. It was observed for these samples that the mechanical property values are decreasing. For example the tensile strength, % elongation and the hardness of these samples were 5.4 MPa, 275 % elongation and 78 Shore A respectively.

All data collected for the SBS system are summarized in Figures 62-63 and Table 11. But it should be mentioned here that no statement has been done for this system at the moment since it needs a futher and detailed study. But it is worth to say that this system have very interesting characteristics as mentioned above.

|  | TENSILE STRENGTH (MPa) | ELONGATION % AT BREAK | HARDNESS SHORE A |  |
|---|---|---|---|---|
| UNFILLED | 14 | 900 | 77.5 |  |
| BAUXITE | 22 | 1450 | 80 |  |
| PPS COATED BAUXITE | 22 | 1450 | 30 |  |
| PPB COATED BAUXITE | 19 | 1450 | 80 |  |
| CARBON BLACK (5 phr) | 25 | 1500 | 79 | without sulfur |
| PPS COATED CARBON BLACK (5 phr) | 25 | 1500 | 79 | without sulfur |
| PPB COATED CARBON BLACK (5 phr) | 25 | 1500 | 79 | without sulfur |
| CARBON BLACK (5 phr) with sulfur | 8.5 | 385 | 80 | 1.15 min at 35 rpm then 30 sec. 20 and 30 sec. 40 rpm. |
| CARBON BLACK (5 phr) with sulfur | 5.4 | 275 | 78 | 2.0 min at 45 rpm then 30 sec. 20 and 30 sec. 40 rpm. |

Table.11. Complete data of SBS Kraton 1101 system

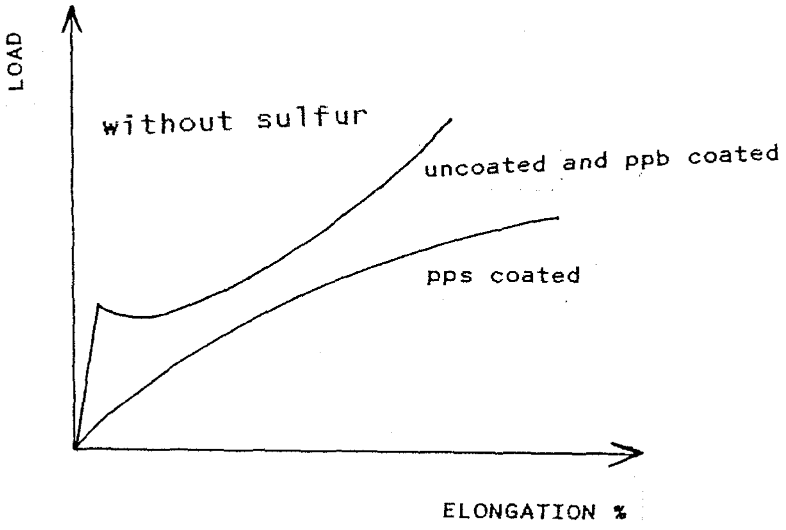


Fig.62. SBS with 35 parts bauxite system

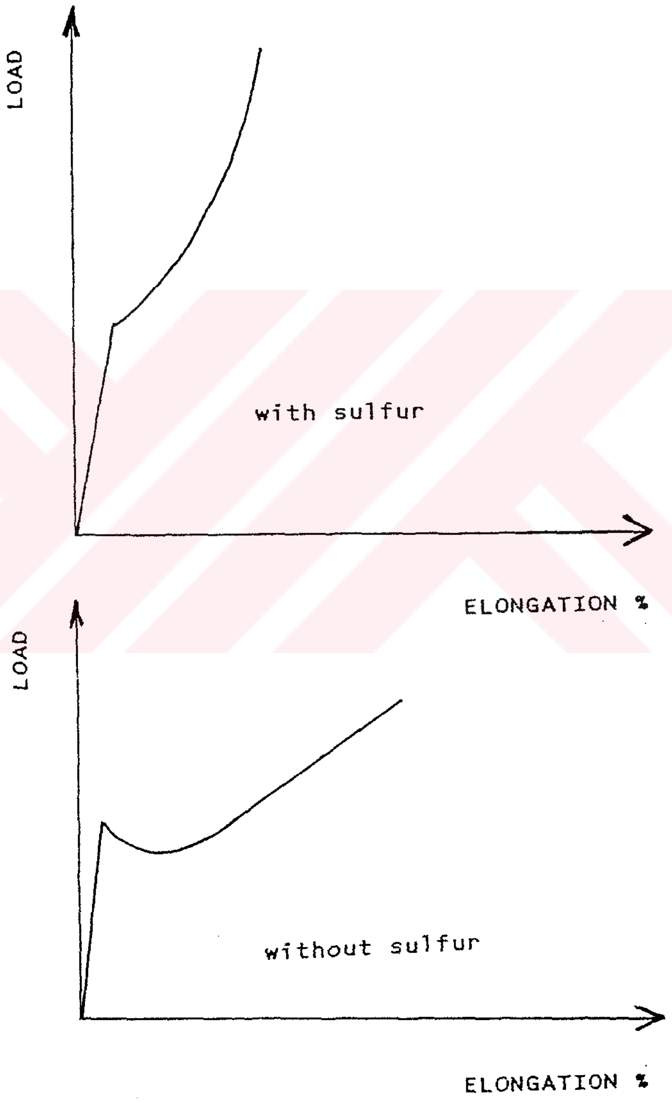


Fig.63. SBS with 5 parts carbon black system

# CONCLUSIONS

It has been concluded that :

1. Bauxite and carbon black surfaces can be modified by plasma polymerization of styrene and butadiene.

2. Plasma polymerization technique on surface modification of fillers has promising advantages since both surface selectivity and structure effects of fillers can be used simultaneously for better adhesion due to the thinness of the coatings obtained by this technique.

3. Cure kinetics can be affected by surface modification of fillers.

4. pps and ppb coated carbon black filled rubbers have extraordinary advantages since it is both possible to increase the tensile strength (more strong) while decreasing the hardness (due to pps coating), or to decrease the tensile strength (weak) while increasing the hardness of the vulcanizates.

5. Large amount of saving can be gained by this technique since it may be possible to get the desired properties of the

5. Large amount of saving can be gained by this technique since it may be possible to get the desired properties of the rubber vulcanizates by using lesser amounts of carbon black and/or chain extender especially during tire manufacture.

6. Finally it has been concluded that this technique can present additional chances to adjust the mechanical properties especially when it was thought as an alternative to set the filler/oil ratio during compounding rubbers because it compensates the opposite effects of oil and filler additions.

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