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THE ADHESION OF SILICA REINFORCED NATURAL RUBBER TO POLYETHYLENE--ETC(U)  
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**REPORT 667**

**THE ADHESION OF SILICA REINFORCED NATURAL RUBBER  
TO POLYETHYLENE**

C. E. M. Morris

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TO POLYETHYLENE

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## A B S T R A C T

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The adhesion of natural rubber to polyethylene, using three samples of hydrated silica of different particle size to reinforce the rubber, has been examined. Laminates were made, without an intermediate adhesive layer, by injection or compression moulding, and the adhesion assessed, in the majority of cases, by peel tests, although some tensile and tensile-shear tests were also performed. The strength of adhesion was found to depend on the particle size of the silica and on the physical properties of the rubber samples. An influence of the magnitude of the coefficient of thermal expansion above the glass transition of the rubber samples on the adhesion strength was also noted.

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## THE ADHESION OF SILICA REINFORCED NATURAL

### RUBBER TO POLYETHYLENE

#### 1. INTRODUCTION

In recent years increasing use has been made of adhesive bonding as a means of joining the components in an assembly. Such bonding of organic materials is in general difficult and this has led to a large amount of work being done on factors affecting the adhesion, both with and without adhesives, of polymeric materials.

A preliminary investigation was undertaken some years ago of the adhesion of rubber to polyethylene, the samples being made by injection moulding the polyethylene onto the rubber. This work, by Mr. J. Woodford at MRL, surveyed a considerable number of systems, such as natural rubber in the form of smoked sheet, pale crepe and SMR, and some synthetic rubbers such as styrene-butadiene rubber and butyl, formulated with various carbon blacks, silicas, clay and whiting and also a number of activators such as triethanolamine (1). The bond strength was assessed by means of 90° peel tests. The effect on the peel strength of such factors as surface roughness of the rubber and the length of time between moulding the rubber and bonding it was also considered. Peel strengths covered about a 20-fold range.

A close examination of the results of this survey indicated that in the case of natural rubber, systems reinforced with silica had a higher peel strength from polyethylene than those with the other materials and that fine particle silica gave better results than coarser silicas. Addition of a small amount of a paraffin wax to the fine particle silica reinforced sample gave a further improvement in peel strength. The present programme was undertaken to examine these observations in greater detail with the object of further elucidating the factors which determine the strength of adhesion.

Fine particle reinforcing silicas became available to the rubber industry in the late nineteen forties. Since that time the use of these materials, principally for light coloured compounds, has gradually expanded. The properties of such rubbers, using many different rubber polymers, and the particular compounding requirements, have been extensively investigated (2-4).



A number of examples of improved adhesion with silica and silicate reinforced rubbers has been noted (5). The particular case of partial replacement of carbon black with fine particle reinforcing silica in tyre compounds, and the effect which this has on the adhesion to nylon, rayon, polyester and brass plated wire tyre cords has received considerable attention (6-8). An increase in adhesion was reported (7), particularly in the presence of resin forming additives such as the resorcinol-hexamethylenetetramine combination (3,7-9). Other examples of improved adhesion to polyamide with silica reinforced compounds have been noted for a number of rubbers (10) and for EPDM adhesion to woven nylon duck and brass sheet (4). Conversely it has been reported that no such improvement in adhesion occurs with butyl and other non-polar elastomers (8,10).

The whole question of the adhesion of elastomers to a wide variety of substrates has received much attention and the various theories put forward have been reviewed by Crocker (11). Considerable diversity of opinion has been expressed, especially regarding the importance of diffusion controlled processes, as advocated by some Russian workers (12). This controversy arises in large measure from problems relating to the interpretation of test data, since the viscoelastic nature of these materials makes the results far from unequivocal.

The most commonly used test is probably peel as this is appropriate for adhesives testing and for rubber-fabric (tyre cord) adhesion. However, the interpretation of peel test results, in terms of the fundamental processes taking place, is difficult and thus for research purposes other tests, such as tensile, are preferable.

Many attempts have been made to relate peel force to adhesion strength. The arrangement of a thin adhesive layer on a flexible backing being peeled from a rigid substrate has been studied by several workers (13-17) and it has been shown that the effect of adhesive layer thickness, peeling rate and temperature are amenable to the Williams, Landel, Ferry treatment for viscoelastic materials (15,16), although the relations are complex (18).

Recently, the peeling of thin layers of a viscoelastic material from a rigid substrate has been examined closely in an attempt to reconcile the surface chemical and rheological approaches to the question of the cause of adhesion strength (or weakness). In the surface chemical approach considerable attention has been directed to the importance of wetting of the substrate by the adhesive as a necessary (but perhaps not sufficient) condition for the attainment of high joint strength (19,20). For joints failing at least partly cohesively, the bulk properties of the adhesive, substrate and interfacial phases must also be considered (19,20). The rheological approach focuses on the contribution to adhesive strength arising from rheological losses in the adhesive and substrate, but as the magnitude of these rheological processes depends on such factors as joint geometry and test method, conflicting results have been reported. By careful consideration of the experimental arrangement, it has been shown that, in general, there is an adhesive failure energy, which is characteristic of the bond and independent of the joint geometry, and which consists of two components, one arising from the physical and chemical nature of the adhesive-substrate interface and the other from the deformation of the adhesive during separation (21-24). The relative magnitude of the contributions of these two

factors to the total adhesive joint strength has been examined for a number of cases (23,24). Similar conclusions on the existence of a characteristic adhesive failure energy have been reached from tensile and shear tests (24,25).

The role of the bulk properties of elastomeric adhesives has been examined in terms of the effect of vulcanisation time (degree of cure) (26-28) and cross link density (29). The Russian workers interpreted their results in terms of diffusion processes across the interface, whereas the more recent results have been discussed in terms of the rheological loss properties of the rubber.

Thus, significant advances have been made in recent years in the understanding of the theoretical basis of the adhesion of elastomeric adhesives to rigid substrates as assessed by peel testing. Although the combined effects of surface chemical and rheological factors have been demonstrated, the very complexity of these effects, particularly the influence on the latter of joint geometry and test method, means that it is not yet possible to predict adhesion strength in a given practical situation.

## 2. MATERIALS

Two grades of natural rubber were used, SMR 5 (Standard Malaysian Rubber) and SMR 5L which differ only in that the latter is of a lighter colour. Three hydrated silicas of different reinforcing ability were employed, Ultrasil VN3, Hi Sil 233 and Neosyl Std., at various loadings up to 65 parts per hundred parts of rubber, by weight (phr). The first two of these are regarded as highly reinforcing fillers and the third as only mildly so. Some of their chemical and physical properties are shown in Table 1. The vulcanising system was a typical sulphur-accelerator combination. Details of these, of other compounding ingredients and formulations are given in Appendix 1.

The initial part of this study used the Woodford formulations. Each batch was made separately in a Midget Banbury internal mixer and the calculated amount of accelerators added on a 2 roll mill (300 mm x 500 mm). Later batches, formulation numbers 582C and higher, which were modifications of the earlier formulations and which minimised as far as possible the number of ingredients, were made by masterbatching procedures. The mixing was done either in a Banbury or on a mill, and the accelerators then added on the mill.

A sample of each batch mixed was cured in a Monsanto Oscillating Disc Rheometer (model LSD), using a small rotor (capacity about 5 g), a 3° arc at 300 Hz at 146°C, in order to determine cure characteristics. The rest of the batch was then cured in a press (at 146°C and about 350 MPa pressure) in the form of sheets approximately 250 mm x 125 mm and about 1.75 mm thick. Drawn polyester film (approx. 0.05 mm thick) was used as the only mould release agent. The cured sheets were stored between the polyester film until required.

Each batch was characterised by tensile strength, modulus at 300% elongation, elongation at break and hardness measurements. The first three of these properties were measured on either a Frank testing machine, model 652, or an Instron tensometer, model 1026, using dumbbell shaped test specimens, dimensions 6.3 mm wide x 285 mm long over the narrow centre section and 19.0 mm x 17.5 mm at the ends with a total length of 97 mm. The specimens were aged for at least 24 h at 22°C before testing. The rate of elongation was 500 mm/min. Hardness (IRHD) was determined with a Wallace dead load hardness tester. The physical test data for all rubbers used are given in Appendix 1.

The earlier formulations were characterised by short cure times (a few minutes at 146°C), a tendency to reversion and the products, especially those with high silica loadings, had poor mechanical properties, particularly tensile strength. All later formulations contained 2% by weight (based on the silica) of a poly(ethylene glycol) activator which reduced the reversion, lengthened the cure time (to the range 5-7 min) and improved the physical properties. Glycol or amine activators are required to minimise a secondary reaction of the vulcanising system with the silica (2,32). Details are given in Appendix 2 of the effect on the cure characteristics and physical properties of the poly(ethylene glycol) content and of variations in the vulcanising system, both of these being examined to optimise physical properties.

The effect on the physical properties of the change from rubber grade SMR 5 to SMR 5L and of the addition of small amounts of a paraffin wax were also considered (Appendix 2). Incorporation of this wax is normally made to improve resistance to sunlight, but earlier work indicated that its addition had a beneficial effect on the adhesion to polyethylene (1). In general, only small changes to the physical properties resulted from these modifications.

The polyethylene used was Hostalen G 7260, a high density polyethylene supplied by Hoechst Australia Ltd. Plaques (usually 125 x 75 x 1.5 mm) were injection moulded on a Netstal SM 60/40, ram type, 95 g capacity machine using a nozzle temperature of 200°C, injection pressure 4.0 MPa, dwell time 20 sec and a cooling time of 30 sec. No heating or cooling was applied to the mould. Compression moulding of samples was performed using a Pasadena Hydraulics Press, model 0-230-H, fitted with water cooled, electrically heated platens.

### 3. SURFACE STUDIES

Considerable efforts were directed towards characterising the physical and chemical nature of the surface of the rubber, particularly differences between various rubber samples. Infra-red studies, using the ATR method, were not possible as the silica absorbed strongly over a large proportion of the IR region. The factors studied were therefore surface roughness and the critical surface tension of wetting.



### 3.1 Surface Roughness

Surface roughness was assessed by means of Talysurf traces, contact angles and scanning electron microscopy.

Talysurf traces were run on a model 4 instrument. These measurements were not wholly satisfactory as the surface asperities were distorted by the traverse of the stylus, thereby furnishing a modified trace of the surface roughness. The ratio profile length/nominal length of the trace was taken as a measure of the roughness. Two different rubber samples were assessed, part of each being deliberately roughened by wire brushing. The value of the ratio ranged from about 3 to 8. Static contact angles of water were measured at a number of places on the surface corresponding to the regions over which Talysurf traces were run. It was found that a small increase in contact angle occurred with increasing roughness ratio and that, in general, wire brushed surfaces showed higher contact angles than unbrushed surfaces (Table 2). In view of the well documented effects of roughness on contact angles this effect is smaller than was expected. It may well be that there is a directional effect on the wire brushed surfaces, i.e., spreading of a liquid along the troughs may be easier than across, which results in brushing appearing to have only a small effect.

The surface of a number of samples containing different silicas, both as moulded and after buffing on a grinding wheel, was examined by means of a Stereoscan Series II scanning electron microscope using a tilt angle of  $45^\circ$  and magnifications up to about 1800. The as moulded samples were almost completely featureless, but for the buffed surfaces, while small areas appeared fairly smooth, most of the surface was rough and some areas had a distinctly stringy appearance. Representative micrographs are shown in Fig. 1.

### 3.2 Critical Surface Tension of Wetting

The critical surface tension of wetting was determined for several rubbers as a means of characterising the chemical nature of the surface. Advancing, receding and static contact angles were measured, with liquids of different surface tension, by the use of a stage, which could be tilted to any angle, and a travelling microscope fitted with a goniometer eyepiece. The procedure was to mount the rubber sample on the stage, place a drop of the test liquid on the sample and, while viewing the drop through the microscope, tilt the stage until the drop was on the point of moving. The contact angle ( $\theta$ ) was then measured, the mean of a number of such determinations being used. Static contact angles were measured with the stage horizontal. The liquids were chosen to cover a wide range of surface tensions and to be inert with respect to the rubber, which meant using water and glycol derivatives, ranging in surface tension from 33 to  $63 \times 10^{-3}$  N/m, (measured on a du Nouy tensometer calibrated with distilled water). The polar force contribution to the total surface free energy of such a series of liquids varies considerably, which is a disadvantage for this application. Representative results for the advancing contact angles are shown in Table 3. The critical surface tension of wetting was determined by plotting  $\cos \theta$  vs surface tension of the liquid and extrapolating to  $\cos \theta = 1$  ( $\theta = 0$ ). Although there is some scatter in the results, little difference is apparent between the various rubbers. Thus, the critical surface tension of wetting



is about  $25 \times 10^{-3}$  N/m and is independent of the presence in the rubber of paraffin wax and of different silicas. Similar conclusions were drawn from the static and receding contact angle measurements.

#### 4. THERMAL ANALYSIS

A comparison was made of the glass transition temperature,  $T_g$ , and the linear coefficient of thermal expansion above and below  $T_g$  ( $B_L$  and  $B_g$  respectively) of the unreinforced rubber and the rubbers containing 60 phr and 30 phr of the three silicas (formulations 582C, 583C and D, 586A and B and 587A and B). The results (Table 4) were obtained from TMA studies determined with a du Pont model 941 Thermomechanical Analyzer, using a heating rate of  $5^\circ\text{C}/\text{min}$  and a flat tipped (2.5 mm diameter) probe loaded to about 0.1 g.

The strongly reinforcing fillers, Ultrasil VN3 and Hi Sil 233, have a significant influence on  $T_g$  and  $B_L$ , whereas the slightly reinforcing Neosyl Std. has a lesser effect. The coefficient of expansion below  $T_g$  is almost unaffected by the silica type and loading.

#### 5. ADHESION TESTING

The assessment of different methods of measuring adhesion strength required the manufacture of test specimens of various geometries and the development of special techniques. In some instances the method proved to be inappropriate while in others satisfactory test pieces could not be made.

##### 5.1 Tensile Tests

Initial experiments concerned the measurement of adhesion strength by tensile tests using rubber - PE - rubber laminates made by injection moulding. A special mould insert was made, which incorporated a submarine gate, enabling plaques approx. 75 mm x 65 mm x 10 mm to be moulded. Sheets of rubber, about 1.75 mm thick, and cut to the appropriate size, were fixed to the top and bottom of the mould with double sided adhesive tape. The mould was then closed and the PE injected between the rubber sheets to give a PE inter-layer about 6 mm thick. This procedure was difficult as PE sometimes penetrated behind the rubber and distortion of the laminates frequently occurred on cooling.

Circular test specimens were then cut from the laminates. The PE layer prevented the use of stamping or spinning cutters and meant resorting to a band saw, which made it difficult to avoid putting nicks and irregularities in the edges of the test pieces.

The test specimens were bonded to metal end pieces of the same diameter. The adhesive used was a standard two pack, general purpose epoxy resin. The assembly was held inside a short length of tightly fitting PE tube while the adhesive cured in an oven at  $60^\circ\text{C}$  for an hour. Initial

trials with a methyl cyanoacrylate adhesive were unsatisfactory as this material has poor gap-filling qualities.

Tensile tests were performed on a vertically mounted Hounsfield tensometer equipped with a linear vertical displacement transformer (LVDT). Stretching of the rubber during the test causes a stress concentrating effect (4) (Fig. 2(a) and (b)) and, since the peel force is much less than the tensile strength of such an arrangement, there was a tendency for an edge imperfection to act as an initiating site for peel, resulting in the assembly failing in peel. Use of larger specimens (38 mm diameter instead of 25 mm), thinner rubber (down to 0.64 mm) and a harder testing machine reduced the magnitude of this problem. Measurements were also made with square test pieces, (20 mm x 20 mm) as these could more easily be cut without edge imperfections, but peel could not be entirely eliminated.

The results, given in Table 5, show that the failure load of the laminates increased with decreasing rubber thickness. This effect has been found in other adhesively bonded butt joints (33,34). The failure load was in fact inversely proportional to the thickness (Fig. 3), in agreement with the analysis of Gent for viscoelastic systems where the radius of the test piece is large compared with the thickness (25).

The possibility of using PE - rubber - PE laminates was considered. Test specimens could be made by compression moulding. However, the difficulties attendant on surface treating the PE to permit bonding of the metal end pieces were such as to eliminate this arrangement.

## 5.2 Tensile-Shear Tests

Tensile-shear tests on lap joints were examined and the limiting factor proved to be manufacture of suitable test specimens. It was necessary for the PE to be on the outside and gripped in the jaws of the testing machine.

Single lap joints 25 mm wide with 25 mm bonded overlap could be made by compression moulding using inserts, such as Teflon-coated paper, to limit the PE-rubber bonding to specific areas. However, during testing, the PE bent thereby putting the bond line at an angle to the force direction. Any point of weakness would then act as an initiating site and the assembly would fail in peel (Fig. 2(c) and (d)).

The fabrication of double lap joints proved difficult and one example, made by compression moulding, is shown in Fig. 4(a). The bonded area consisted of five layers while the rest of the mould space was filled with pieces of metal wrapped in Teflon coated paper. The thickness was limited by the depth of the available mould (about 7 mm). Production of specimens by an injection moulding technique, while possible, was difficult.

When these laminates were tested it was found that it was still possible for the PE to bend resulting in peel (Fig. 4(b)). Although this effect could be modified by alteration of the dimensions of the various layers, the practical difficulties in the manufacture of suitable test pieces were deemed to be such that tensile-shear tests were abandoned.

### 5.3 Peel Tests

Test pieces from earlier rubbers (up to 583C) were made in the form of rubber - PE - rubber laminates, approx. 125 mm x 75 mm x 7 mm by compression moulding. This entailed a significant amount of time in the mould at about 200°C, as heat had to be transferred through the rubber to the PE. Since these formulations suffered from reversion and were somewhat under-cured, as they contained no poly(ethylene glycol), this reheating to temperatures higher than the original cure temperature resulted in a further decrease in physical properties (approx. a 10-15% reduction in tensile strength for example). Test pieces with later formulations (583C and above) were made in the form of rubber - PE laminates by injection moulding, the rubber sheet being held in the bottom of the mould with double sided adhesive tape and the PE injected on top.

Cuts were made through the rubber (but not the PE substrate) in such a way that narrow strips (2-3 mm) were removed from between the 19 mm wide test strips, thereby minimising the effect of a test on the adjacent strip. 90° peel tests were performed with an Instron model 1026 testing machine using a crosshead separation rate of 50 mm/min. The laminates were mounted on a specially constructed trolley which ensured that the peel angle remained close to 90°. The laminate was turned through 180° between each test so that adjacent strips were peeled in opposite directions. Peel strength determinations were made at least in triplicate.

The chart trace of the peeling was an irregular array of peaks and troughs reflecting the complexity of peel tests on elastomeric systems, (Fig. 5). Consideration of the situation in the region of separation of the two layers indicates that there is a zone of compression of the rubber in front of the advancing point of separation, a force inwards from the edges of the strip tending to lift them up and that the radius of curvature of the peeled strip is dependent on the rubber stiffness and the load, (Fig. 6(a) and (b)). In addition, the peeling can be considered to proceed in a series of small jerks, since as a section of rubber peels it is free to stretch, the peeling force momentarily drops and then rises again to peel the next small section. Thus a series of peaks and troughs in the trace is to be expected, quite apart from local variations in the strength of the adhesion. An average value of the peaks was taken as the peel force.

The time dependence of the observed peel force was not examined. The intervals between moulding the rubber sheets and injecting on the PE and then performing the peel tests was similar, as far as this was possible.

#### 5.3.1 Effect of Silica Type and Loading on Peel Force

Table 6 shows the average peel force for rubbers containing different loadings of the three silicas. In general, for a given silica loading the peel force is higher the smaller the particle size and for a given particle size is higher the higher the silica loading. Failure in all cases appeared to be adhesive except where otherwise noted.

The peel force of the earlier rubbers, which contained no poly(ethylene glycol), was higher than that obtained with the later materials. This is



in agreement with results of other workers who found that the addition of glycols, while greatly improving the physical properties of the rubbers, reduces the adhesion to other materials (8).

### 5.3.2 Addition of Paraffin Wax

Earlier work suggested that the addition of small amounts of a paraffin wax, normally incorporated to improve resistance to sunlight, increased the peel force (1). A number of rubbers were made to investigate this, the results being given in Table 6. Although the paraffin wax would bloom to the surface, it did not materially alter the critical surface tension of wetting of the surface (Table 3).

From Table 6 it is seen that in the earlier rubbers, which contained no poly(ethylene glycol), the addition of a paraffin wax had a significant, beneficial effect on the peel strength. This improvement was not evident in the later rubbers. This is apparently another manifestation of the adverse effect of glycols on adhesion. In one experiment, a small amount of melted paraffin wax was spread on the surface of a rubber which contained no wax, (569E), allowed to solidify and the rubber laminated to PE. A reduction in peel strength of approx. 40% was observed. This is an example of the weak boundary layer effect.

### 5.3.3 Correlation with Physical Properties

The data in Table 6 indicate that for a given silica loading the peel force varies by about a factor of five for the three silicas examined. Since the various techniques used to examine the physical and chemical nature of the surfaces of the rubbers indicated no significant differences between them, explanation of the observed peel force range was sought in terms of the physical properties of these rubbers. Fig. 7-10 show the relationship between peel force and modulus at 300% elongation, tensile strength, elongation at break and hardness for the rubbers in Table 6 at 30 and 60 phr silica loading. (For values of these properties see Appendix 1). The results show, in general, that for a given silica loading the peel strength decreases with increasing 300% modulus, but increases with increasing tensile strength, elongation at break and hardness.

## 6. DISCUSSION

In the present work the observed differences in peel force between the various systems cover a wide range. This is not simply a result of differences in either the chemical or physical nature of the surfaces of these systems. Indeed, there is evidence that textural differences, arising from deliberate roughening, are not utilised as a possible keying mechanism. Presumably the PE, when injected on to roughened surfaces, cools and solidifies too rapidly to be able to penetrate into these interstices in the rubber surface. Alternatively, the rubber may be too soft to provide an effective lock so that on application of a small load the PE pulls out. However, as the peeled PE surfaces generally appeared smooth and glossy, it seems likely that penetration into the rubber surface did not occur.



The contact angle data show that the surface of the various rubbers is essentially the same with respect to its wettability, thereby indicating that on the basis of the wetting theory of adhesion, no difference in the strength of adhesion would be expected. The effect of weak boundary layers as a possible source of variations in the adhesive strength is clearly discernible in the case of the paraffin wax on the surface. Diffusion controlled processes, known to be significant in the bonding of some rubber systems, are unlikely to be so in the present case as the two phases in contact are so dissimilar. Furthermore, the time interval between the various steps was kept approximately constant. All later rubbers were made by masterbatching and so closely related systems had a similar processing history. Thus the time intervals, while varying slightly between such groups, were constant within a group. In addition, a number of rubbers were made and tested twice. It is, however, possible that diffusion processes contributed to the experimental scatter.

From these considerations it appears unlikely that the observed differences in peel strength arise from surface chemical or topographical factors.

The data in Table 6 indicate that the peel force is dependent on the silica particle size and this relationship is shown in Fig. 11, where the particle size is given in terms of the surface area of silica per 100 parts of rubber, (Table 1). As Neosyl Std. has only mildly reinforcing properties, it seems that the aggregates are not broken up during compounding and that consequently a large proportion of the surface area measured by the BET method is not accessible to the rubber polymer. Thus the surface area which is available for interaction with the rubber has been calculated by taking the particle size of the aggregates, assumed to be spherical, as 1  $\mu$ m diameter, which gives a surface area of 1.5 m<sup>2</sup>/g. Such a calculation is in error to the extent that it ignores the effect of particle size distribution, but it does enable the overall relationship between effective silica surface area and other factors to be depicted.

The data in Fig. 7-10 show that the peel force is also related to various physical properties of the rubber, such as tensile strength and modulus, but also that the results for the two silica loadings fall on two distinct curves. Fig. 12 shows the dependence of the modulus at 300% elongation on the effective silica surface area. For a given silica loading the modulus decreases with decreasing particle size (increasing surface area) and also for a given silica the modulus increases with loading, in agreement with previous findings (2). Similar curves for tensile strength show that tensile strength increases with decreasing particle size at a particular loading and for a given silica passes through a shallow maximum with increasing silica loading (2).

Thus for a given silica loading the peel force appears to be dependent on the silica particle size via the effect which the particle size has on the bulk physical properties of the rubber. However, other factors are also important.

Thermal analysis showed that both  $T_g$  and the coefficient of thermal expansion in the rubbery state,  $B_L$ , were significantly changed by the presence of silica, (Table 4). Little work has been reported on the effect of reinforcing fillers on  $T_g$  and the coefficients of expansion of

elastomers (35). It has been claimed (35,36) that in a butadiene-styrene copolymer MT carbon black (specific surface area  $7 \text{ m}^2/\text{g}$ ) had no effect on  $T_g$  but that with HAF carbon black (specific surface area  $80 \text{ m}^2/\text{g}$ ) an increase in  $T_g$  was observed with increasing black loading. No change was found in the coefficient of expansion in the rubbery region but in the glassy region the coefficient of expansion decreased with increasing black loading. No effect on  $T_g$  was reported for natural rubber with MT and HAF blacks up to 18% volume loading (37). These findings are at variance with the present results for silica reinforced rubbers and indicate that further thermo-analytical studies are warranted.

With unreinforced rubbers, it has been reported (26-29) that at a constant test temperature the peel force increases as the intercrosslink molecular weight decreases (and hence  $T_g$  increases). The interpretation given to these results is that as  $T_g$  increases more energy is expended in viscoelastic deformations at the failure site (28,29). At high cross link densities shrinkage stresses, giving rise to a zone of high stress adjacent to the substrate, which could cause a decrease in the observed peel force, must be considered (26,38).

In the present case, the largest decrease in  $T_g$  was shown by those rubbers which contained the larger amounts of strongly reinforcing fillers, and which showed the highest peel force. A correlation exists between  $B_L$  and the peel force whereby the peel force is higher the smaller is the coefficient of thermal expansion (Fig. 13), which probably is a manifestation of the effects of shrinkage stresses at the rubber-PE interface. These peel test specimens were made by injecting the molten PE on to the rubber which was at room temperature. Evidently, those rubbers with the smallest coefficient of thermal expansion resulted in peel test specimens with smaller levels of frozen in stresses at the interface, and this was a contributing factor in the higher peel force displayed.

## 7. CONCLUSIONS

In the adhesion of silica-reinforced natural rubber to polyethylene, without an intermediate adhesive layer, the particle size of the silica exerted a considerable influence on the strength of the adhesion. This difference in adhesion resulted from the effect of the silica particle size on the bulk properties of the rubber, particularly tensile strength and modulus at 300% elongation. Differences in the silica type and loading also changed certain thermal properties, especially the coefficient of thermal expansion above the glass transition temperature, which in turn affected the level of frozen in stress at the rubber-polyethylene interface when the samples were made by injection moulding. Surface chemical and surface roughness effects made little, if any, contribution to the adhesive strength. Undercured rubbers, while showing improved adhesion, had poor physical properties, especially tensile strength.

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T A B L E 1

## PROPERTIES OF SILICA SAMPLES

Property	Ultrasil VN3(a,b)	Hi Sil 233(a,b)	Neosyl Std(a,c)
Ultimate Particle Size, nm	16	22	100-200(d)
Surface Area(e), m <sup>2</sup> /g	234	150	120-380
Specific Gravity	1.9-2.0	2.0	2.0
SiO <sub>2</sub> , % by weight	87	88	83
Weight Loss at 105°C, %	5	5	10
pH, 10% Aqueous Suspension	6	7	8

(a) See Table 9

(b) Reference 30

(c) Reference 31

(d) Aggregating to 1-10  $\mu$ m(e) N<sub>2</sub> adsorption, BET method

T A B L E 2

EFFECT OF SURFACE ROUGHNESS<sup>(a)</sup> ON CONTACT ANGLE

Roughness Ratio <sup>(b)</sup>	Contact Angle of Water	
	Wire Brushed	Unbrushed
4.0	126°	135°
7.0	136°	140°

(a) Formulation 573C

(b) See Section 3.1 for definition of roughness ratio.

T A B L E 3

## CONTACT ANGLES FOR A RANGE OF LIQUIDS ON VARIOUS RUBBER SURFACES

Liquids	Surface Tension $\times 10^{-3}$ , N/m	Advancing Contact Angles, degrees					
		582C (a)	569E (b)	583C (c)	586A (d)	587A (e)	585A <sub>3</sub> (g)
Dipropylene glycol	33	59	56	58	54	61	58
Propylene glycol	36	64	72	71	67	74	77
Ethylene oxide-propylene oxide copolymer	37	66	71	64	67	73	79
Poly(ethylene glycol)	44	76	86	70	75	76	88
Glycerol	64	-	94	-	-	-	93
Water	72	92	98	105	90	86	103

- (a) No reinforcing agent.  
 (b) 65 phr Ultrasil VN3, no poly(ethylene glycol) activator.  
 (c) 60 phr Ultrasil VN3.  
 (d) 60 phr Hi Sil 233.  
 (e) 60 phr Neosyl Std.  
 (f) As 569E plus 3 phr paraffin wax.  
 (g) As 583C plus 4 phr paraffin wax.



T A B L E 4

THERMAL ANALYSIS DATA OF VULCANISED RUBBERS

Property	Not reinforced (582C)	Ultrasil 60 phr (583C)	Hi Sil 60 phr (586A)	Neosyl 60 phr (587A)	Ultrasil 30 phr (583D)	Hi Sil 30 phr (586B)	Neosyl 30 phr (587B)
Glass Transition Temperature, $T_g$ , °C	-56	-64	-64	-62	-60	-60	-60
Decomposition Temperature, $T_d$ , °C	100	110	115	-	120	140	140
Coefficient of Thermal Expansion below $T_g$ , $B_g$ , $10^{-4} K^{-1}$	1.0	0.7	0.7	0.7	0.8	0.7	0.7
Coefficient of Thermal Expansion above $T_g$ , $B_L$ , $10^{-4} K^{-1}$	2.75	0.70	0.75	2.0	2.0	2.1	2.4

T A B L E 5

EFFECT OF RUBBER THICKNESS ON TENSILE FAILURE LOAD  
OF RUBBER-PE-RUBBER LAMINATES

Rubber Thickness, mm	Tensile Failure Load,* kN
2.8	2.1
1.5	2.3
1.0	2.8
0.6	3.4

\* Circular test pieces, as in Fig. 2(a), diameter 25 mm.  
Mean of 4 determinations. Formulation No. 573C.

TABLE 6

EFFECT OF SILICA TYPE AND LOADING AND OF THE ADDITION  
OF PARAFFIN WAX ON THE PEEL FORCE

Amount of Paraffin Wax, phr	Peel Force, N, <sup>(a)</sup> and Formulation Number		
	Ultrasil VN3	H1 Sil 233	Neosyl Std.
	<u>Silica Loading 60 phr</u>		
-	39 (583C)	35 (586A)	10 (587A)
1	47 (585A <sub>1</sub> )	32 (586A <sub>1</sub> )	11 (587A <sub>1</sub> )
2	45 (585A <sub>2</sub> )	35 (586A <sub>2</sub> )	10 (587A <sub>2</sub> )
4	38 (585A <sub>3</sub> )	29 (586A <sub>3</sub> )	11 (587A <sub>3</sub> )
	<u>Silica Loading 30 phr</u>		
-	17 (583D)	8 (586B)	3 (587B)
1	9 (585B <sub>1</sub> )	13 (586B <sub>1</sub> )	4 (587B <sub>1</sub> )
2	10 (585B <sub>2</sub> )	10 (586B <sub>2</sub> )	5 (587B <sub>2</sub> )
4	17 (585B <sub>3</sub> )	14 (586B <sub>3</sub> )	4 (587B <sub>3</sub> )
	<u>Silica Loading 65 phr <sup>(b)</sup></u>		
-	71 <sup>(c)</sup> (569E)	93 (571B)	28 (571A)
1	>130 <sup>(d)</sup> (580B)	-	-
2	>130 <sup>(d)</sup> (580A)	-	-
4	>140 <sup>(d)</sup> (580C)	-	-
	<u>No Silica</u>		
-	-	1 <sup>(e)</sup> (582C)	-

(a) For strips 19 mm wide. Peel force accuracy, in all cases, approx.  $\pm 1N$ .

(b) These formulations contained no activator and the test specimens were made by compression moulding, i.e. poor physical properties.

(c) Peel force with paraffin wax melted on surface (see text) 44N.

(d) Cohesive failure of the rubber.

(e) Effectively no adhesion.



As Moulded



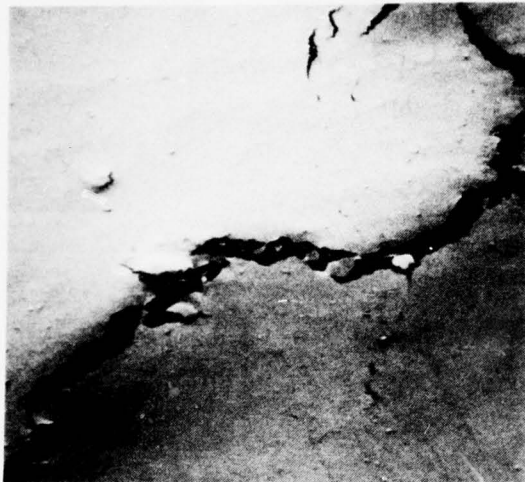
Wire Brushed



Ultrasil VN3 65 phr. x1120



Hi Sil 233 65 phr. x1760



Neosyl Std. 65 phr. x1760

FIG. 1 - Scanning electron micrographs of rubber surfaces in the as moulded and wire brushed states.

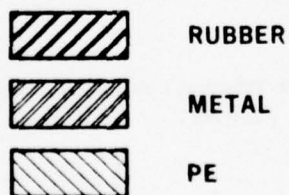
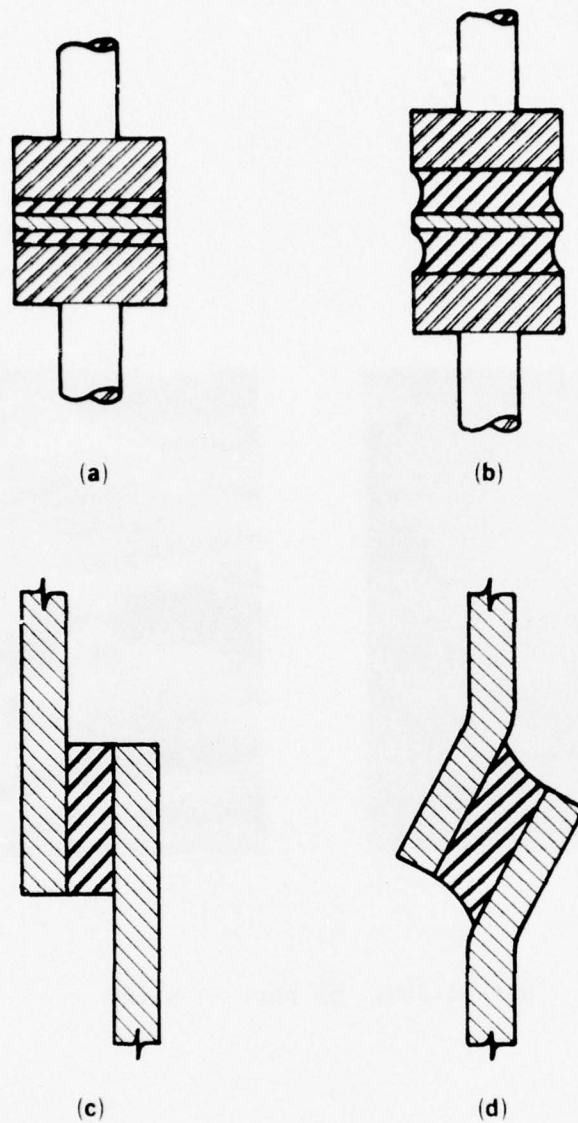


FIG. 2 - Schematic representation of joints in the unloaded and loaded states.

(a) and (b) butt joints.  
 (c) and (d) single lap joints.



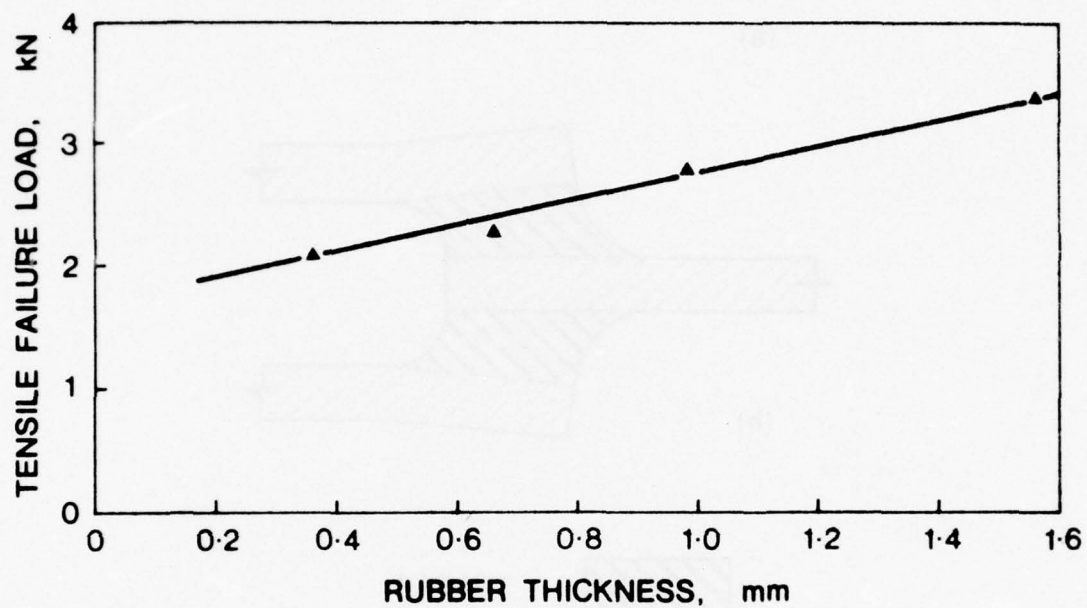
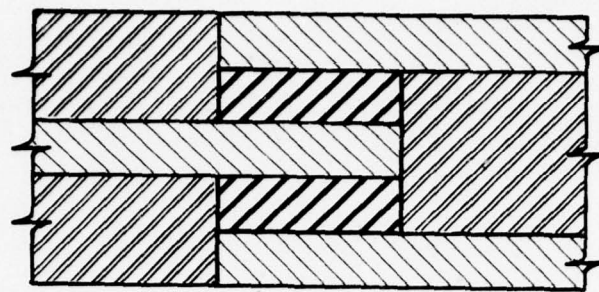
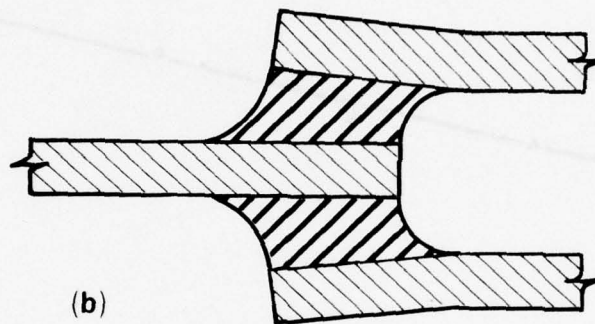


FIG. 3 - The dependence of the tensile failure load on the rubber thickness for circular butt joints.



(a)



(b)



RUBBER



METAL



PE

FIG. 4 - Schematic representation of double lap joints.

(a) configuration moulded.

(b) loaded specimen.

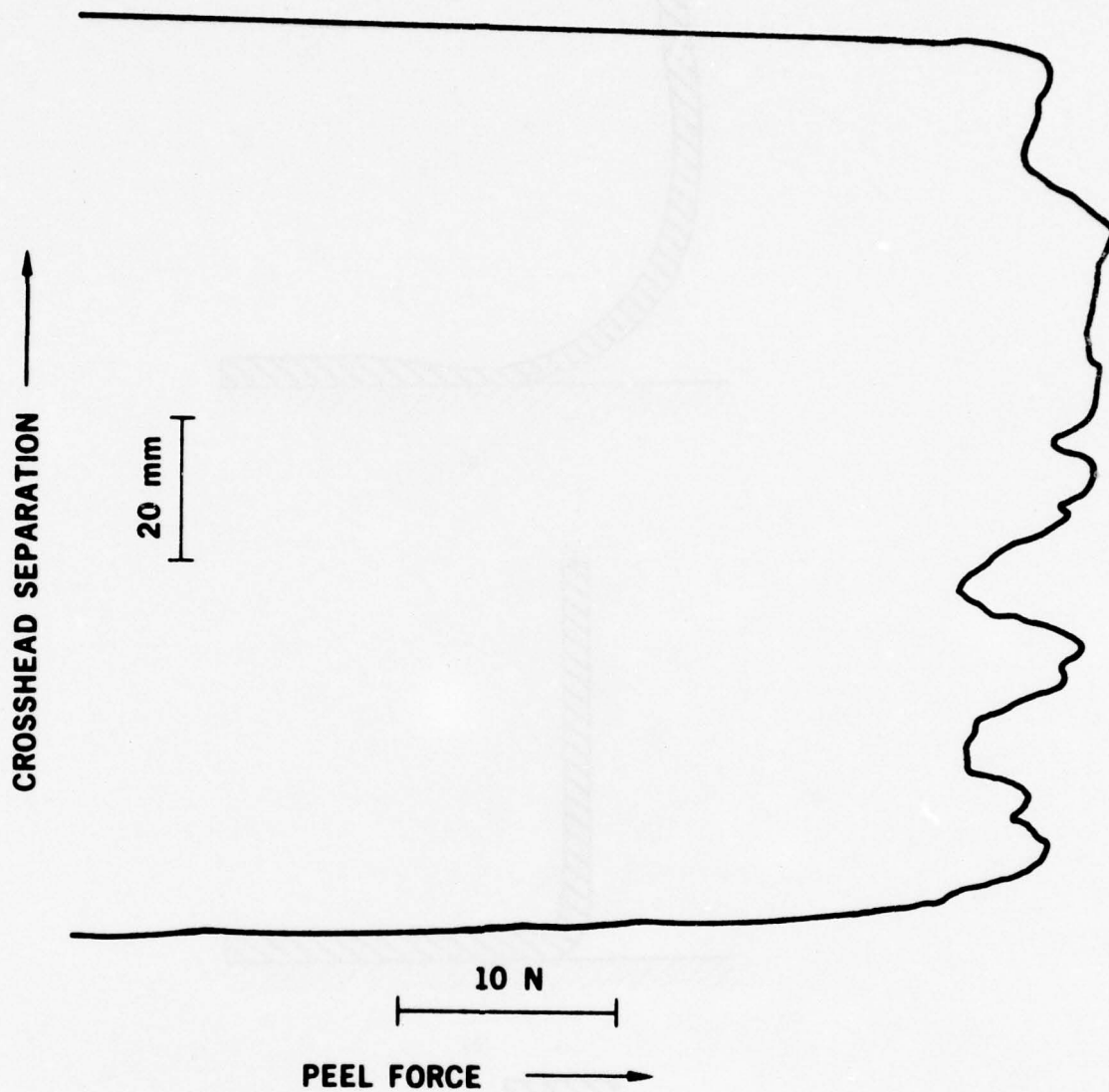
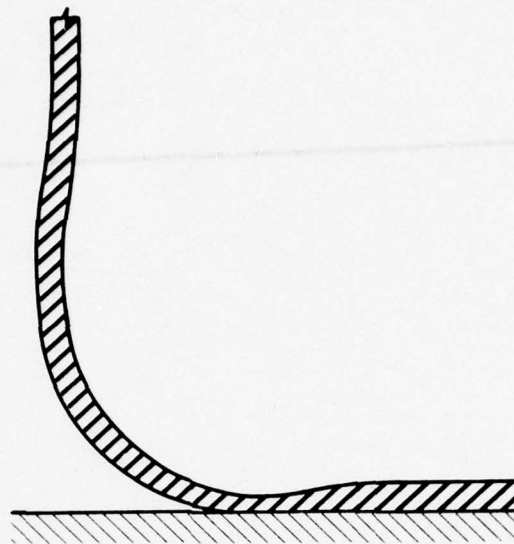
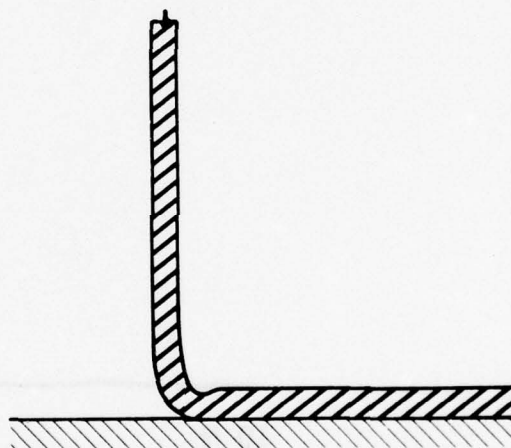


FIG. 5 - Representative trace of a peel test.





(a)



(b)



RUBBER



PE

FIG. 6 - Schematic representation of a peel test.

(a) stiff rubber at low loads.

(b) stiff rubber at high loads and  
soft rubber at all loads.

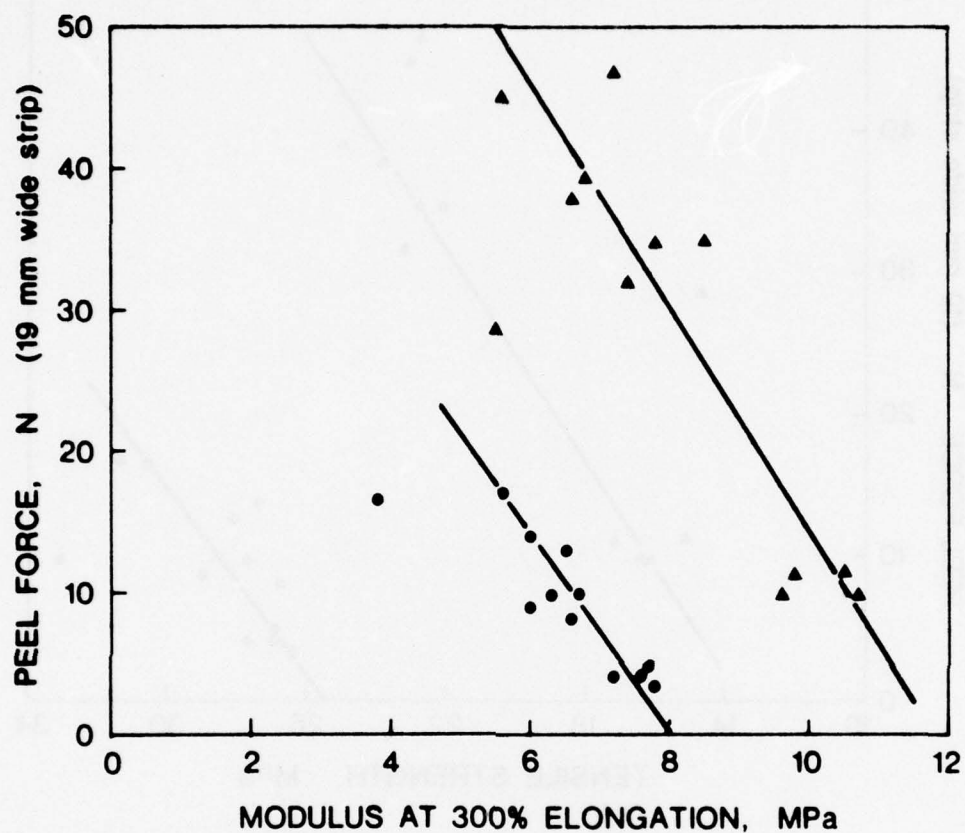


FIG. 7 - Relationship between peel force and modulus at 300% elongation of the rubber.

- 30 phr silica loading;
- ▲ 60 phr silica loading.

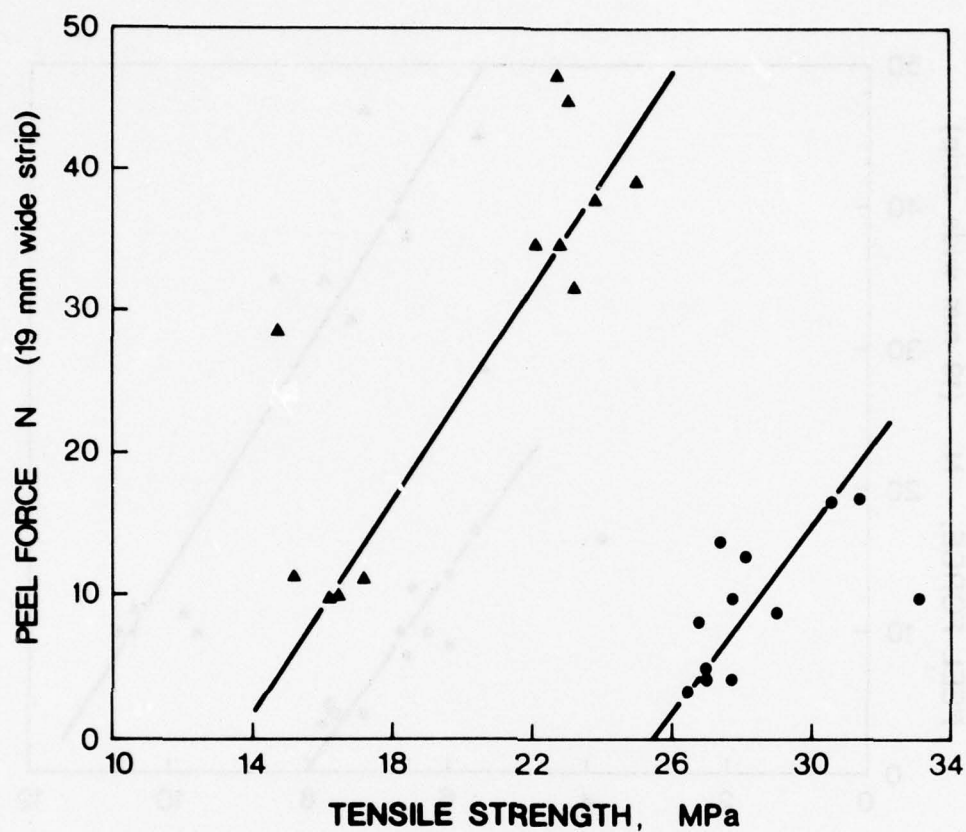


FIG. 8 - Relationship between peel force and tensile strength of the rubber.

- 30 phr silica loading;
- ▲ 60 phr silica loading.



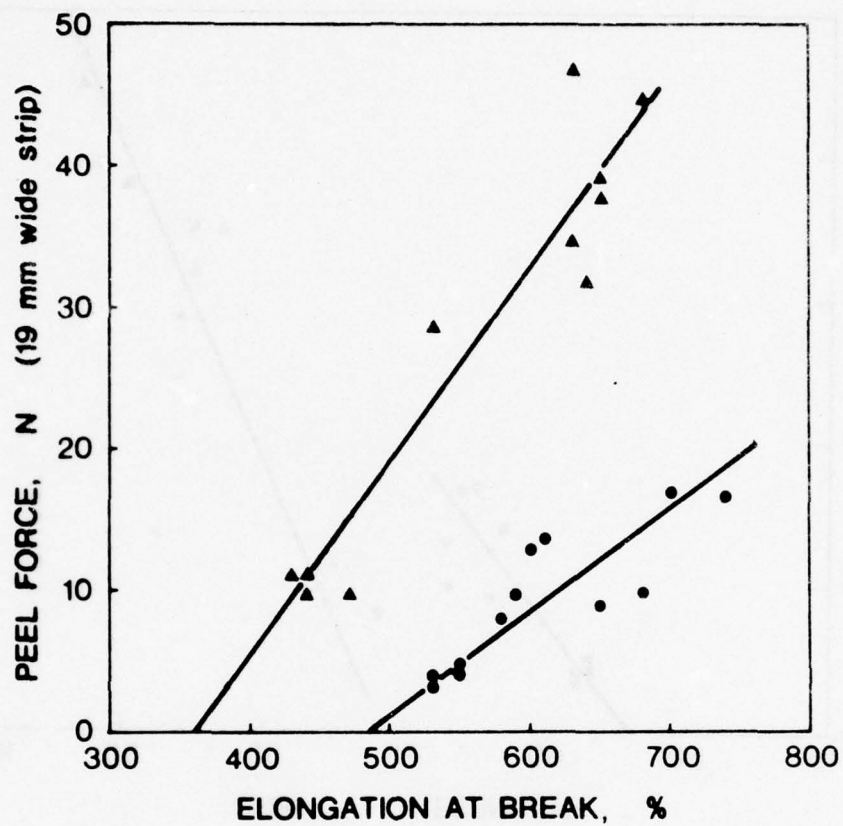


FIG. 9 - Relationship between peel force and elongation at break of the rubber.

- 30 phr silica loading;
- ▲ 60 phr silica loading.

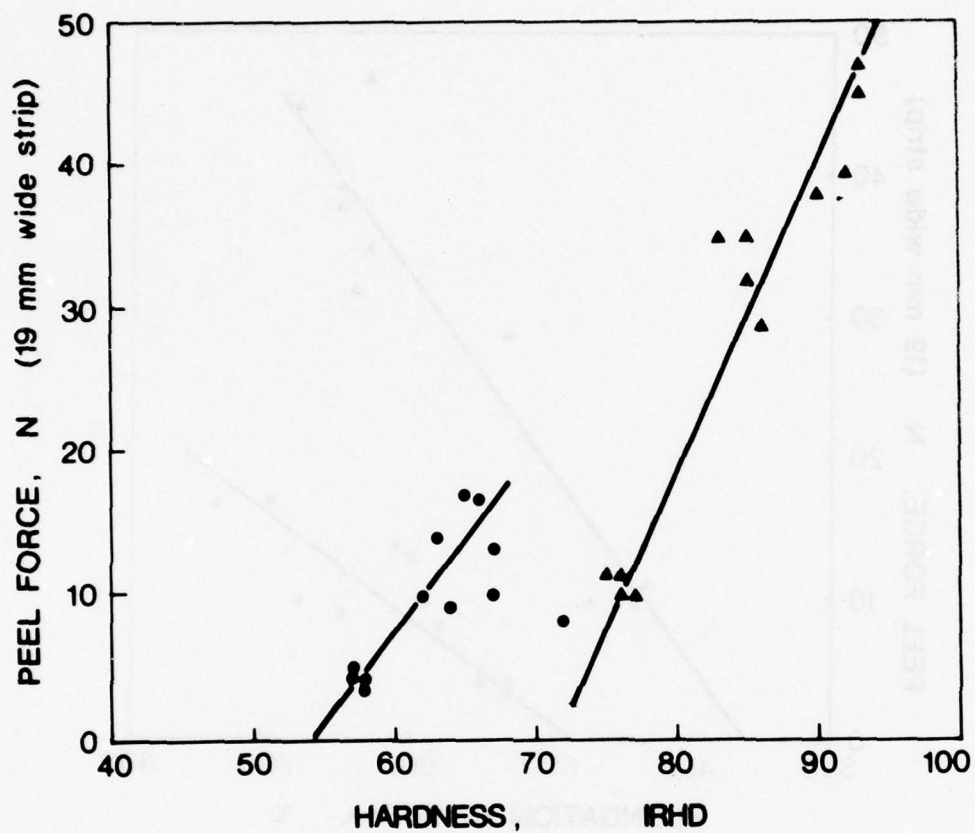


FIG. 10 - Relationship between peel force and hardness of the rubber.

- 30 phr silica loading;
- ▲ 60 phr silica loading.

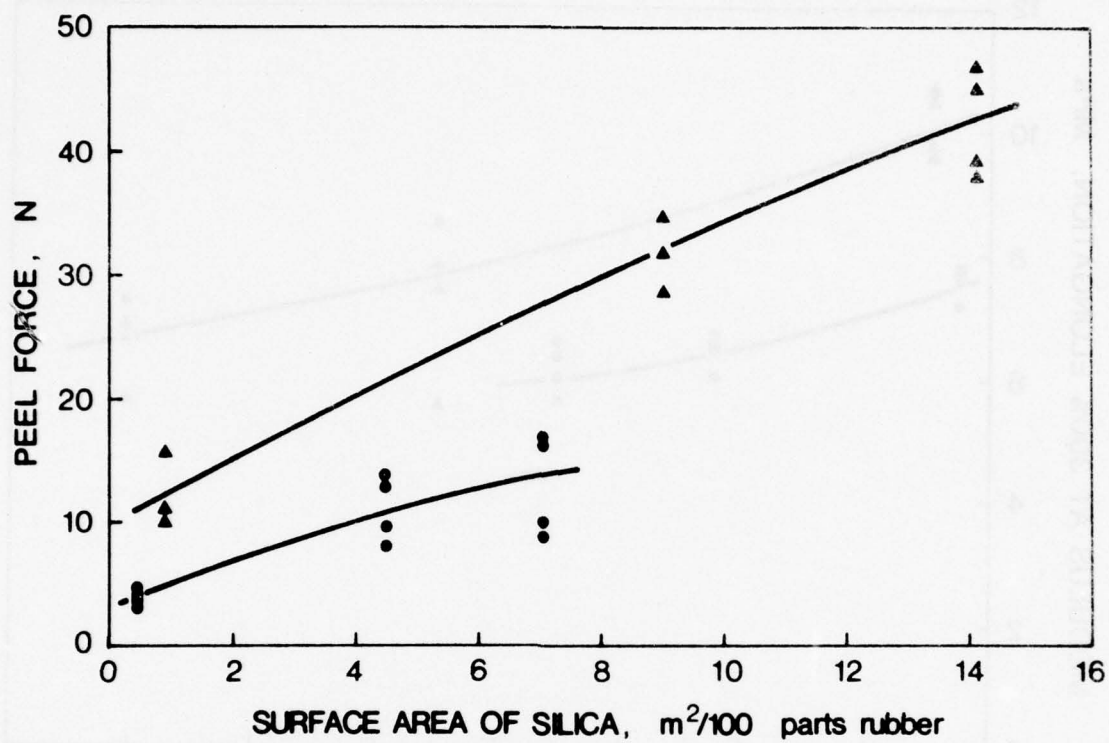


FIG. 11 - Relationship between peel force and the surface area of the silica.

- 30 phr silica;
- ▲ 60 phr silica.



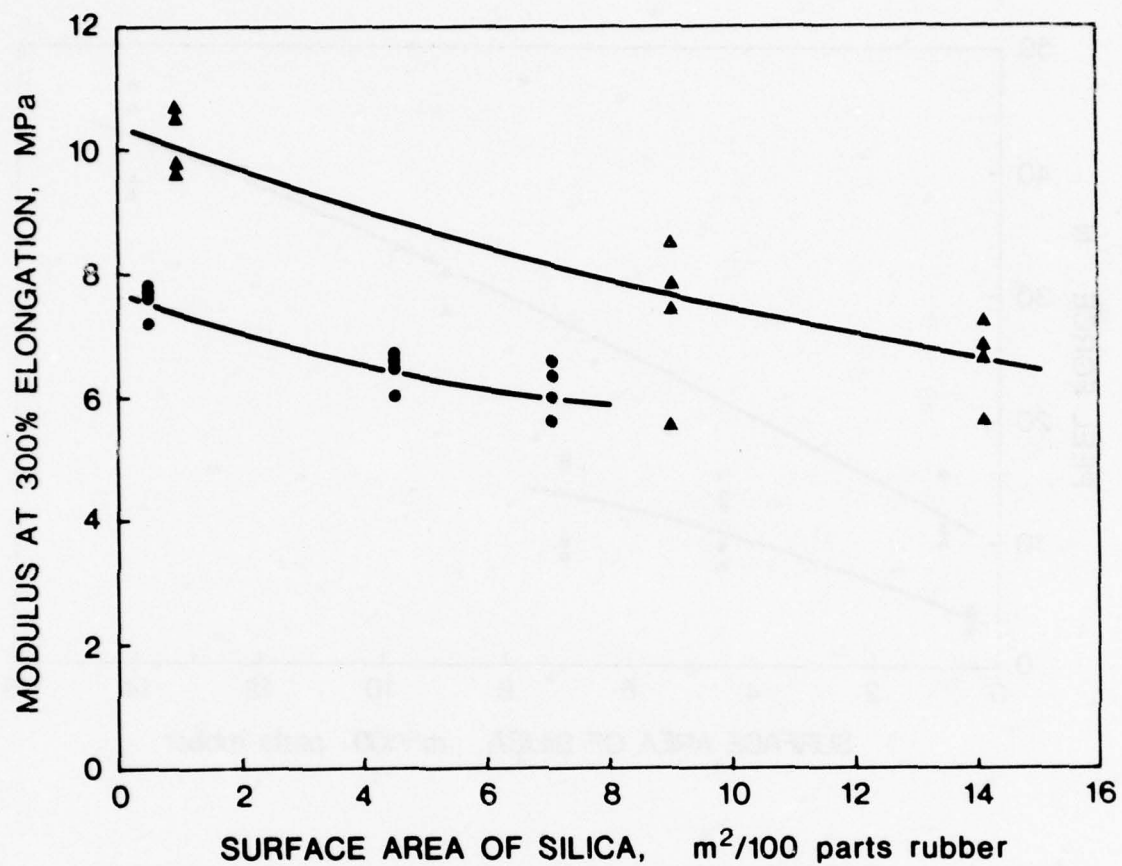


FIG. 12 - Relationship between the modulus at 300% elongation of the rubber and the surface area of the silica.

• 30 phr silica;

▲ 60 phr silica.

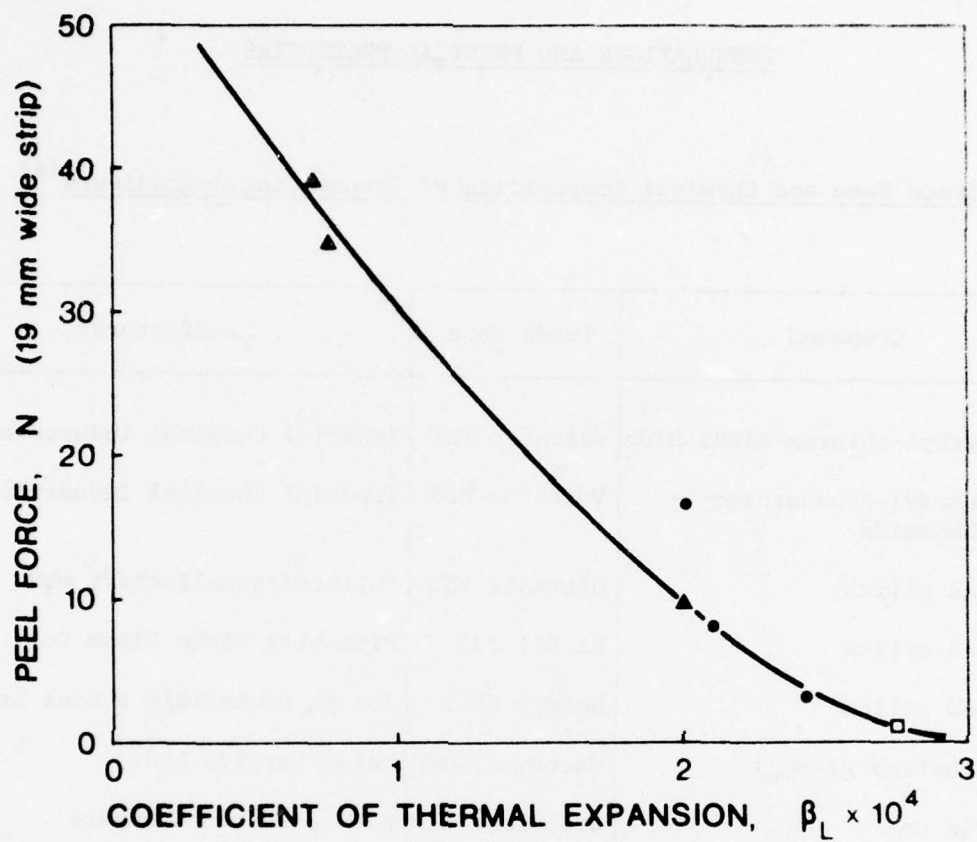


FIG. 13 - The peel force as a function of the coefficient of thermal expansion in the rubbery region of the rubber.

- 30 phr silica;
- ▲ 60 phr silica;
- no silica.

APPENDIX 1

FORMULATIONS AND PHYSICAL PROPERTIES

Trade Name and Chemical Composition of Compounding Ingredients<sup>(a)</sup>

Compound	Trade Name	Manufacturer
Tetramethyl-thiuram-disulphide	Vulcafor TMT	Imperial Chemical Industries Ltd.
N-cyclohexyl-2-benzthiazyl-sulphenamide	Vulcafor HBS	Imperial Chemical Industries Ltd.
Hydrated silica	Ultrasil VN3	Fullstoffgesellschaft mbH
Hydrated silica	Hi Sil 233	Pittsburg Plate Glass Co.
Hydrated silica	Neosyl Std.	Joseph Crossfield & Sons Ltd.
Poly(ethylene glycol)	Carbowax 4000	Union Carbide Ltd.
Paraffin wax	Heliozone wax	E.I. duPont de Nemours
Phenyl- $\beta$ -naphthylamine	Nonox D	Imperial Chemical Industries Ltd.

(a) These particular compounds were used as they were readily available. No significance should be ascribed to their use in place of similar products or other manufacturers.

Formulation and Physical Properties of Rubbers

Formulation No.	569E	571A	571B	573C
SMR 5	100	100	100	100
Silica, Ultrasil VN3	65	-	-	65
Hi Sil 233	-	-	65	-
Neosyl Std.	-	65	-	-
Paraffin Wax	-	-	-	3
Zinc Oxide	3	3	3	3
Stearic Acid	2	2	2	2
Phenyl- $\beta$ -naphthylamine	1.5	1.5	1.5	1.5
Tetramethyl-thiuram-disulphide	1.25	1.25	1.25	1.25
N-cyclohexyl-2-benzthiazyl-sulphenamide	0.5	0.5	0.5	0.5
Sulphur	1.5	1.5	1.5	1.5
Modulus at 300%, MPa	6.5	7.9	7.2	7.5
Tensile Strength, MPa	12.8	10.8	22.3	14.3
Elongation at Break, %	500	420	630	460
Hardness, IRHD	92	66	90	87
Formulation No.	580A	580B	580C	582C
SMR 5	100	100	100	100
Silica, Ultrasil VN3	65	65	65	-
Paraffin Wax	2	1	4	-
Zinc Oxide	3	3	3	3
Stearic Acid	2	2	2	2
Phenyl- $\beta$ -naphthylamine	1.5	1.5	1.5	1.5
Tetramethyl-thiuram-disulphide	1.25	1.25	1.25	1.25
N-cyclohexyl-2-benzthiazyl-sulphenamide	0.5	0.5	0.5	0.5
Sulphur	1.5	1.5	1.5	1.5
Modulus at 300%, MPa	6.1	5.5	3.9	3.9
Tensile Strength, MPa	12.8	16.1	11.2	24.8
Elongation at Break, %	520	630	600	470
Hardness, IRHD	92	91	90	47



Formulation No.	583A	583B	583C	583D	583D <sub>1</sub>	583D <sub>2</sub>
SMR 5	100	100	100	100	100	100
Silica, Ultrasil VN3	60	30	60	30	30	30
Poly(ethylene glycol)	-	-	1.2	0.6	0.6	0.6
Zinc Oxide	3	3	3	3	3	3
Stearic Acid	2	2	2	2	2	2
Tetramethyl-thiuram-disulphide	1.25	1.25	1.25	1.25	1.25	1.25
N-cyclohexyl-2-benzthiazyl sulphenamide	0.5	0.5	0.5	0.5	0.5	0.5
Sulphur	1.5	1.5	1.5	1.5	2.0	1.25
Modulus at 300%, MPa	4.7	2.9	6.8	3.8	3.2	2.5
Tensile Strength, MPa	16.0	26.2	25.0	30.6	27.4	25.5
Elongation at Break, %	620	730	650	740	740	760
Hardness, IRHD	84	56	92	66	58	53
Formulation No.	583D <sub>3</sub>	583D <sub>4</sub>	584A	584A <sub>1</sub>	584B	584B <sub>1</sub>
SMR 5	100	100	100	100	100	100
Silica, Ultrasil VN3	30	30	60	60	30	30
Poly(ethylene glycol)	0.6	0.6	2.4	4.8	1.2	2.4
Zinc Oxide	3	3	3	3	3	3
Stearic Acid	2	2	2	2	2	2
Tetramethyl-thiuram-disulphide	1.0	1.5	1.25	1.25	1.25	1.25
N-cyclohexyl-2-benzthiazyl sulphenamide	0.5	0.5	0.5	0.5	0.5	0.5
Sulphur	1.5	1.5	1.5	1.5	1.5	1.5
Modulus at 300%, MPa	2.4	3.4	3.8	3.6	3.0	3.3
Tensile Strength, MPa	23.3	27.0	19.7	20.4	26.4	27.4
Elongation at Break, %	770	710	700	690	730	700
Hardness, IRHD	51	57	89	87	61	62

Formulation No.	585A <sub>1</sub>	585A <sub>2</sub>	585A <sub>3</sub>	585B <sub>1</sub>	585B <sub>2</sub>	585B <sub>3</sub>
SMR 5L	100	100	100	100	100	100
Silica, Ultrasil VN3	60	60	60	30	30	30
Poly(ethylene glycol)	1.2	1.2	1.2	0.6	0.6	0.6
Paraffin Wax	1	2	4	1	2	4
Zinc Oxide	3	3	3	3	3	3
Stearic Acid	2	2	2	2	2	2
Tetramethyl-thiuram-disulphide	1.25	1.25	1.25	1.25	1.25	1.25
N-cyclohexyl-2-benzthiazyl-sulphenamide	0.5	0.5	0.5	0.5	0.5	0.5
Sulphur	1.5	1.5	1.5	1.5	1.5	1.5
Modulus at 300%, MPa	7.2	5.6	6.6	6.0	6.3	5.6
Tensile Strength, MPa	22.7	23.0	23.8	29.0	33.1	31.4
Elongation at Break, %	630	680	650	650	680	700
Hardness, IRHD	93	93	90	64	62	65
Formulation No.	586A	586A <sub>1</sub>	586A <sub>2</sub>	586A <sub>3</sub>	586B	586B <sub>1</sub>
SMR 5L	100	100	100	100	100	100
Silica, Hi Sil 233	60	60	60	60	30	30
Poly(ethylene glycol)	1.2	1.2	1.2	1.2	0.6	0.6
Paraffin Wax	-	1	2	4	-	1
Zinc Oxide	3	3	3	3	3	3
Stearic Acid	2	2	2	2	2	2
Tetramethyl-thiuram-disulphide	1.25	1.25	1.25	1.25	1.25	1.25
N-cyclohexyl-2-benzthiazyl-sulphenamide	0.5	0.5	0.5	0.5	0.5	0.5
Sulphur	1.5	1.5	1.5	1.5	1.5	1.5
Modulus at 300%, MPa	8.5	7.4	7.8	5.5	6.6	6.5
Tensile Strength, MPa	22.8	23.2	22.1	14.7	26.8	28.1
Elongation at Break, %	630	640	630	530	580	600
Hardness, IRHD	83	85	85	86	72	67

Formulation No.	586B <sub>2</sub>	586B <sub>5</sub>	587A	587A <sub>1</sub>	587A <sub>2</sub>	587A <sub>3</sub>
SMR 5L	100	100	100	100	100	100
Silica, Hi Sil 233	30	30	-	-	-	-
Neosyl Std.	-	-	60	60	60	60
Poly(ethylene glycol)	0.6	0.6	1.2	1.2	1.2	1.2
Paraffin Wax	2	4	-	1	2	4
Zinc Oxide	3	3	3	3	3	3
Stearic Acid	2	2	2	2	2	2
Tetramethyl-thiuram-disulphide	1.25	1.25	1.25	1.25	1.25	1.25
N-cyclohexyl-2-benzthiazyl sulphenamide	0.5	0.5	0.5	0.5	0.5	0.5
Sulphur	1.5	1.5	1.5	1.5	1.5	1.5
Modulus at 300%, MPa	6.7	6.0	10.7	9.8	9.6	10.5
Tensile Strength, MPa	27.8	27.4	16.2	15.2	16.4	17.2
Elongation at Break, %	590	610	440	430	470	440
Hardness, IRHD	67	63	77	76	76	75
Formulation No.	587B	587B <sub>1</sub>	587B <sub>2</sub>	587B <sub>3</sub>		
SMR 5L	100	100	100	100		
Silica, Neosyl Std.	30	30	30	30		
Poly(ethylene glycol)	0.6	0.6	0.6	0.6		
Paraffin Wax	-	1	2	4		
Zinc Oxide	3	3	3	3		
Stearic Acid	2	2	2	2		
Tetramethyl-thiuram-disulphide	1.25	1.25	1.25	1.25		
N-cyclohexyl-2-benzthiazyl-sulphenamide	0.5	0.5	0.5	0.5		
Sulphur	1.5	1.5	1.5	1.5		
Modulus at 300%, MPa	7.8	7.6	7.7	7.2		
Tensile Strength, MPa	26.4	27.0	27.0	27.7		
Elongation at Break, %	530	530	550	550		
Hardness, IRHD	58	58	57	57		



## APPENDIX 2

### EFFECT OF COMPOUNDING VARIATIONS ON CURE CHARACTERISTICS

#### AND PHYSICAL PROPERTIES

##### 1. Poly(ethylene Glycol) Activator

All formulations from 583C onwards contained poly(ethylene glycol) activator and the amount required to give optimum physical properties was examined. The effect which these additions have on such cure characteristics as the time to 90% cure ( $T_{90}$ , taken from rheometer traces) and the extent and rate of reversion was also considered. Table 7 shows the results of incorporation of various amounts of the activator into formulations containing Ultrasil VN3. All subsequent formulations contained 2% by weight poly(ethylene glycol) based on the silica.

The rheometer curves for the formulations containing 60 and 30 phr of the three silicas and 2% poly(ethylene glycol) based on the silica are shown in Fig. 14 and 15. Reversion is still significant with high loadings of the fine particle size silica.

##### 2. Variation of Vulcanising System

The effect on the physical properties and cure time of changes in the accelerator and sulphur loadings were all examined (Table 8).

The vulcanising system used in the earlier formulations was found to be the optimum and its use continued.

##### 3. Addition of a Paraffin Wax

The earlier work of Woodford (1) indicated that the addition of small amounts of a paraffin wax had a beneficial effect on the adhesion. Rheometer traces show (Fig. 16) that such additions modify the cure and also the physical properties slightly, (Appendix 1).

The correlation between the modulus at 300% elongation and the (maximum-minimum) torque on the rheometer traces for the systems containing 60 phr of the three silicas and the paraffin wax is shown in Fig. 17.

##### 4. Change of Rubber Grade

In later formulations, rubber of the grade SMR 5L was used instead of SMR 5. A number of formulations were re-made to assess the difference which this caused and in all cases, while the rheometer torque was somewhat higher, the cure time and physical properties changed to only a small extent (about 10%). By comparison, repetition of the one formulation gave variations of slightly less than 10%.



T A B L E 7

EFFECT OF POLY(ETHYLENE GLYCOL) ACTIVATOR ON THE CURE TIME AND PHYSICAL PROPERTIES

Formulation No.	Poly(ethylene glycol) Content %, by weight, based on silica	Cure Time, T <sub>90</sub> min	Tensile Strength MPa	Modulus, 300% MPa	Elongation at Break %	Hardness IRHD
		<u>60 phr Silica (Ultrasil VN3)</u>				
583A	0	3.25	16.0	4.7	620	84
583C	2	3.75	25.0	6.8	650	92
584A	4	4.0	19.7	3.8	700	89
584A <sub>1</sub>	8	4.75	20.4	3.6	690	87
		<u>30 phr Silica (Ultrasil VN3)</u>				
583B	0	4.75	26.2	2.9	730	56
583D	2	5.75	30.6	3.8	690	58
584B	4	5.50	26.4	3.0	730	61
584B <sub>1</sub>	8	6.25	27.4	3.3	700	62

T A B L E 8

EFFECT OF VARIATIONS OF THE VULCANISING SYSTEM ON THE CURE TIME AND PHYSICAL PROPERTIES

Formulation No.	Variation (a)	Cure Time, T <sub>90</sub> min	Tensile Strength MPa	Modulus, 300% MPa	Elongation at Break %	Hardness IRHD
583D	Basic system	5.75	30.6	3.8	690	58
583D <sub>1</sub>	2.0 phr sulphur	4.25	27.4	3.2	740	58
583D <sub>2</sub>	1.25 phr sulphur	5.0	25.5	2.5	760	53
583D <sub>3</sub>	1.0 phr tetramethyl- thiuram-disulphide	5.0	23.3	2.4	770	51
583D <sub>4</sub>	1.5 phr N-cyclohexyl- 2-benzthiazyl- sulphenamide	4.50	27.0	3.4	710	57

(a) By comparison with the basic system - 1.5 phr sulphur, 1.25 phr tetramethyl-thiuram-disulphide, 0.5 phr N-cyclohexyl-2-benzthiazyl-sulphenamide.

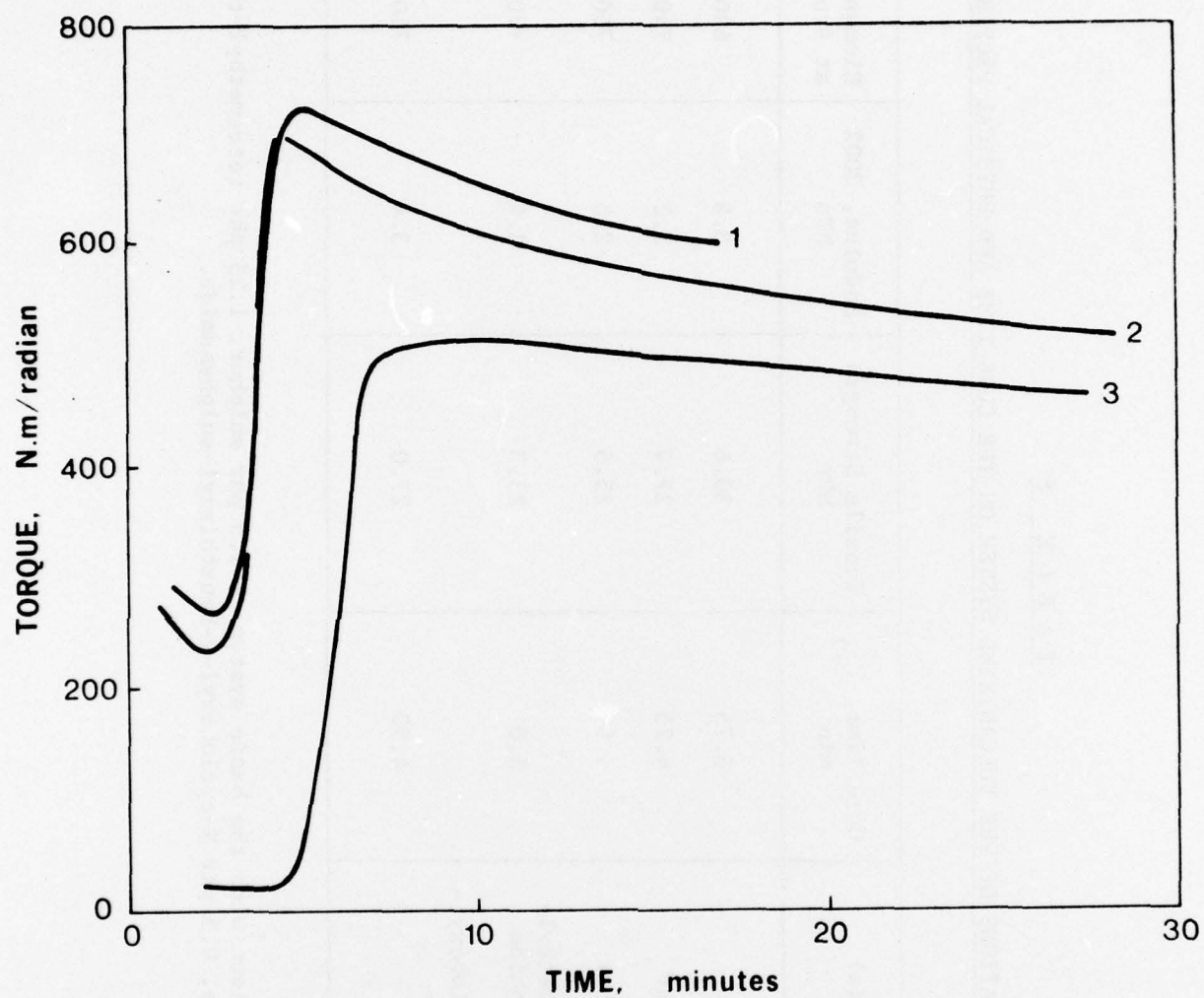


FIG. 14 - Monsanto Rheometer traces of systems containing 60 phr of the three silicas.

1. Ultrasil VN3 (583C);
2. H1 Sil 233 (586A);
3. Neosyl Std. (587A).

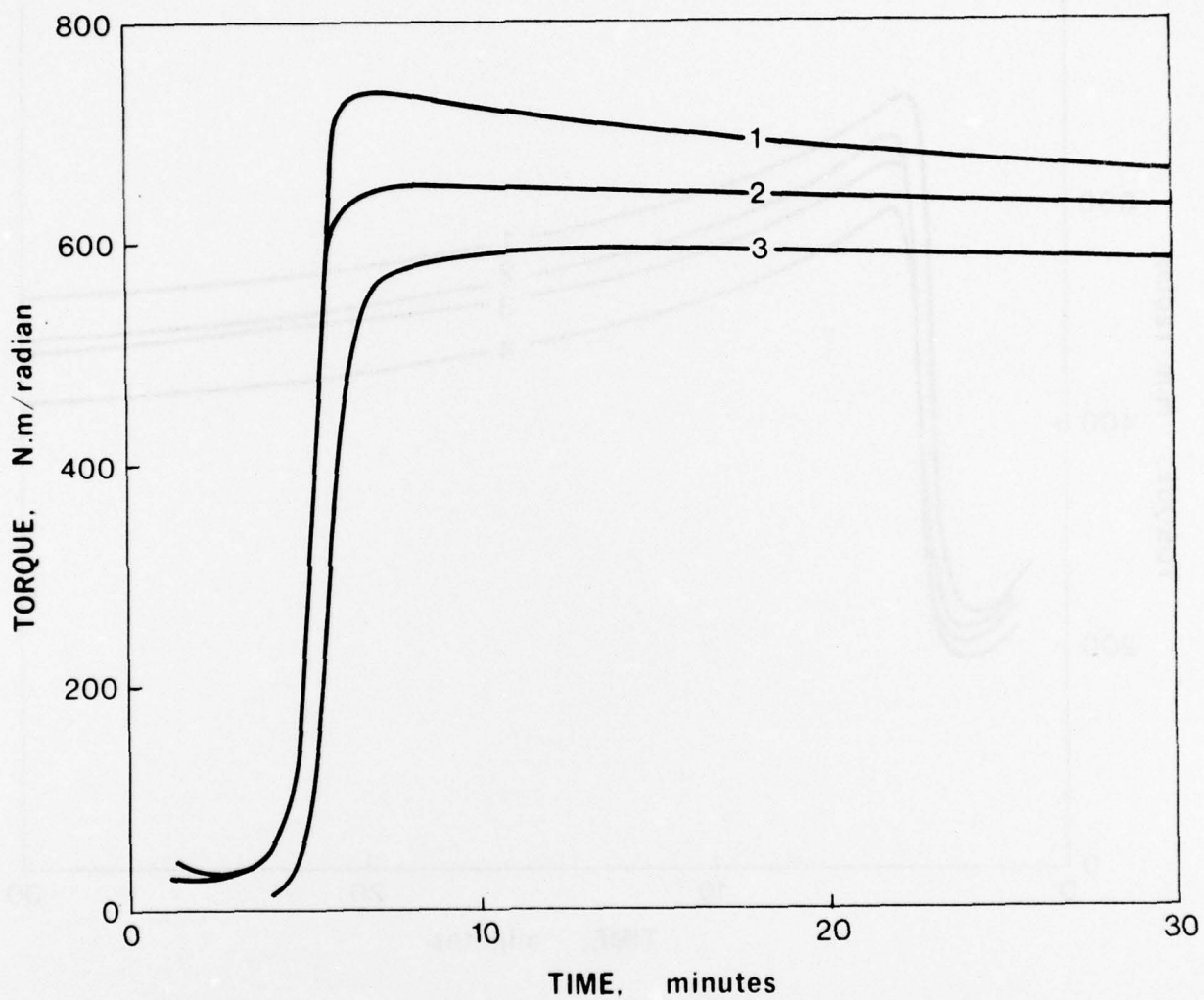


FIG. 15 - Monsanto Rheometer traces of systems containing 30 phr of the three silicas.

1. Ultrasil VN3 (583D);
2. Hi Sil 233 (586B);
3. Neosyl Std. (587B).



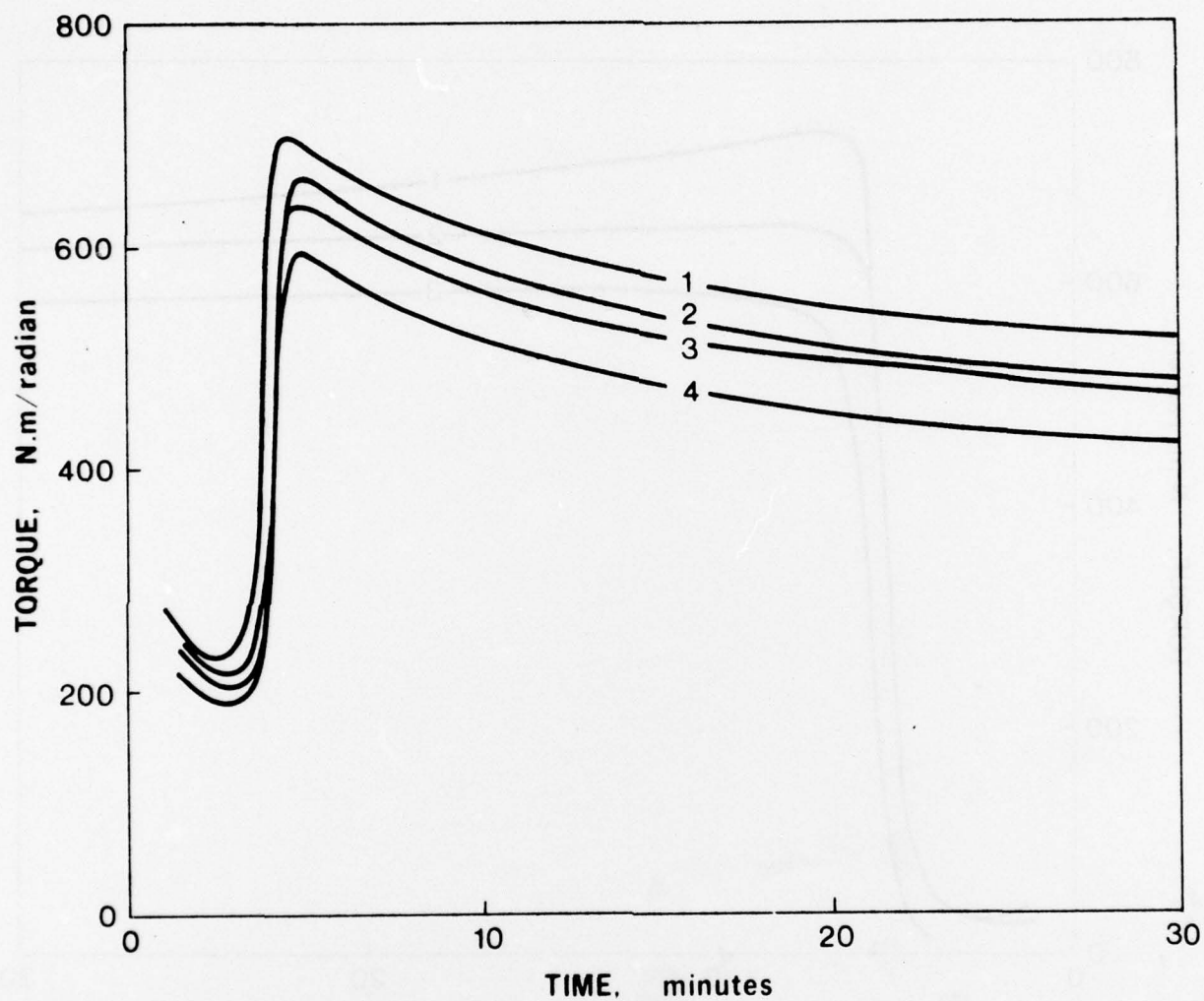


FIG. 16 - The effect of the addition of paraffin wax on the Monsanto Rheometer traces on systems containing 60 phr Hi Sil 233.

1. No wax (586A);
2. 1 phr wax (586A<sub>1</sub>);
3. 2 phr wax (586A<sub>2</sub>);
4. 4 phr wax (586A<sub>3</sub>).

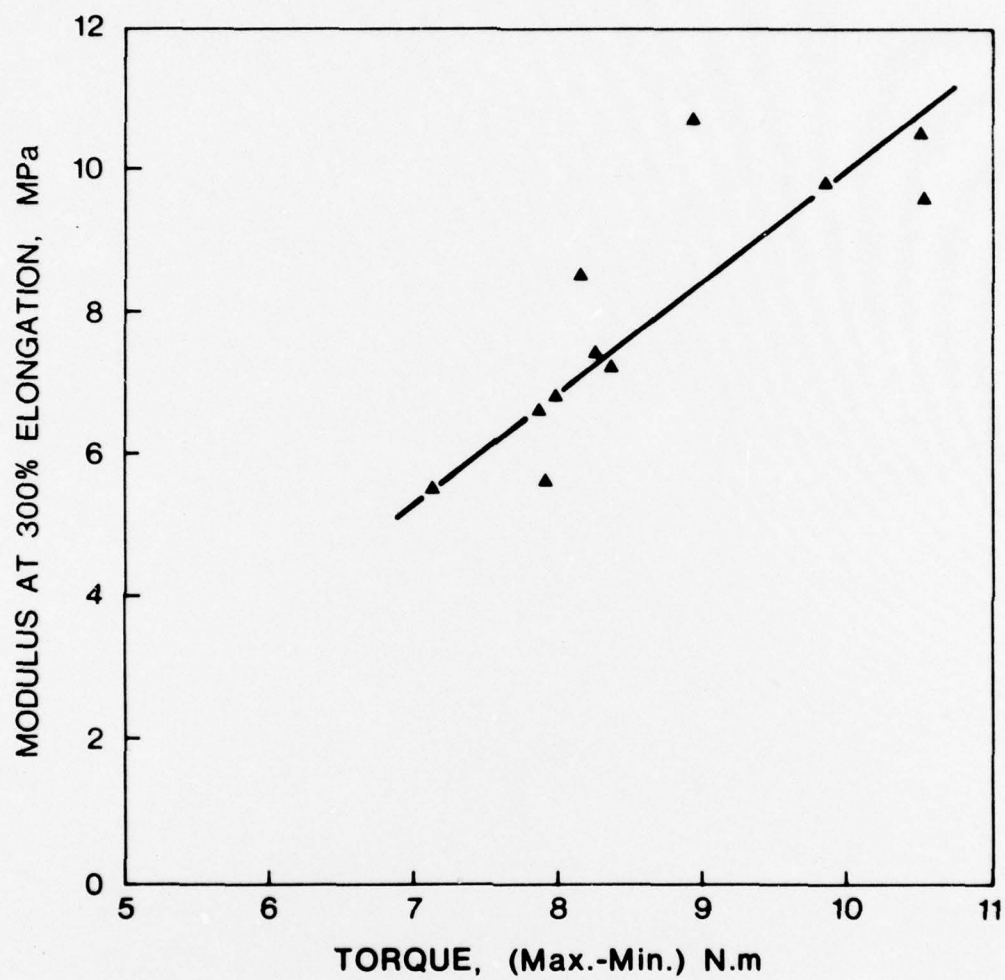


FIG. 17 - The relationship between the modulus at 300% elongation and the (maximum-minimum) torque in the Monsanto Rheometer traces for the systems containing 60 phr of the three silicas.

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