

This article was downloaded by:

On: 22 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



The Journal of Adhesion

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713453635>

Peel Strength of Silica Reinforced Natural Rubber-Polyethylene Laminates

C. E. M. Morris^a

^a Department of Defence, Materials Research Laboratories, Victoria, Australia

To cite this Article Morris, C. E. M.(1978) 'Peel Strength of Silica Reinforced Natural Rubber-Polyethylene Laminates', The Journal of Adhesion, 9: 2, 101 – 113

To link to this Article: DOI: 10.1080/00218467808075105

URL: <http://dx.doi.org/10.1080/00218467808075105>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Peel Strength of Silica Reinforced Natural Rubber-Polyethylene Laminates

C. E. M. MORRIS

Department of Defence, Materials Research Laboratories, Ascot Vale, Victoria, 3032, Australia

(Received September 27, 1976)

The adhesion in silica reinforced natural rubber-polyethylene laminates, made by injection molding without an intermediate adhesive layer, has been examined by means of peel tests. 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, but surface chemical effects made little, if any, contribution to adhesion in these systems.

INTRODUCTION

Fine particle reinforcing silicas became available to the rubber industry in the late 1940s. Since that time the use of these materials, principally for light colored compounds, has gradually expanded. A number of examples of improved adhesion with silica and silicate reinforced rubbers to various substrates has been noted.¹ The partial replacement of carbon black with fine particle reinforcing silica in tire compounds, and the effect which this has on the adhesion to nylon, rayon, polyester and brass-plated steel tire cords, has received considerable attention.²⁻⁴ An increase in adhesion was reported,³ particularly in the presence of resin forming additives such as the resorcinol-hexamethylenetetramine combination.³⁻⁶ Other examples of improved adhesion to polyamide have been noted for a number of rubbers⁷ and for EPDM adhesion to woven nylon duck and brass sheet.⁸ Conversely it has been reported that no such improvement in adhesion occurs with butyl and other non-polar elastomers.^{4, 7}

Various theories of adhesion of elastomers to a wide range of substrates have been reviewed,⁹ the importance of diffusion controlled processes being in dispute.^{9, 10} This arises chiefly from the viscoelastic nature of these materials which makes interpretation of test data far from unequivocal.

Recently the peeling of thin layers of a viscoelastic material from a rigid substrate has been examined closely in an attempt to assess the relative importance of such factors as the wetting of the substrate by the adhesive and rheological losses in the adhesive and substrate. However, as the magnitude of the rheological factors depends in part on joint geometry and test method, conflicting results have been reported. By a 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.¹¹⁻¹⁴ The relative magnitude of the contributions of these two factors to the total adhesive joint strength has been examined for a number of cases.¹³⁻¹⁴ Similar conclusions on the existence of a characteristic adhesive failure energy have been reached from tensile and shear tests.^{14, 15}

Some attention has also been paid to the role of the bulk properties of elastomeric adhesives by examination of the effect of vulcanization time (degree of cure)¹⁶⁻¹⁸ and cross link density.¹⁹ The earlier workers interpreted their results in terms of diffusion processes across the interface, whereas the more recent results have been discussed in the context of rheological loss properties of the rubber.

A brief survey of the peel strength of rubber-PE laminates, using various rubber-filler combinations, indicated that, in the case of natural rubber, systems containing silica had a higher peel strength from PE than those containing other materials,²⁰ 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.^{20, 21} The present program was undertaken to examine these observations in greater detail with the object of further elucidating the factors which determine the strength of adhesion.

EXPERIMENTAL

Two grades of natural rubber were employed, SMR 5 (Standard Malaysian Rubber) and SMR 5L, which differed only in that the latter was of a lighter color. Three hydrated silicas were used, Ultrasil VN3, Hi Sil 233 and Neosyl Std., of which the first two are regarded as highly reinforcing materials and

the third as only mildly so. A comparison of some of their chemical and physical properties is shown in Table I. The vulcanizing system was a typical sulfur-accelerator combination. The formulations were simplified as far as possible to minimize the number of ingredients; details of the formulations are given in the Appendixes.

Formulations were made by masterbatching procedures. The mixing was done either in a midget Banbury internal mixer or on a 2-roll mill and the accelerators added on the mill. A Monsanto Oscillating Disc Rheometer Model LSD was used to determine cure characteristics at 146°C, of each batch. Specimens were then cured in a hydraulic press (at 146°C and about 350 MPa pressure) in the form of sheets approximately 250 mm × 125 mm × 1.75 mm. Drawn polyester film was used in place of a conventional mold release agent and the cured sheets were stored between this film until required.

TABLE I
Some chemical and physical properties of hydrated silicas

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 ² /g)	234	150	120–380
SiO ₂ (%)	87	88	83
Weight loss at 105°C (%)	5	5	10
pH, 10% aq. suspension	6	7	8

^a For details of trade names, see Appendix I.

^b Reference 22.

^c Reference 23.

^d Aggregating to 1–10 μm.

^e N₂ adsorption, BET method.

Each batch of rubber was characterized by tensile strength, modulus at 300% elongation, elongation at break and hardness measurements, using standard techniques. Physical test data for representative vulcanizates are given in Appendix 2.

A simple contact angle apparatus was used to determine the critical surface tension of wetting of the rubber surfaces. The liquids, chosen to cover a wide range of surface tensions and to be inert with respect to the rubber, were a series of glycol derivatives whose surface tensions were determined on a du Nouy tensometer calibrated with distilled water.

Thermal analysis of a number of rubber batches was performed with a du Pont model 941 Thermomechanical Analyzer, using a heating rate of 5°C/min and a flat tipped (2.5 mm diameter) probe loaded to the equivalent of about 0.1 g. The glass transition temperature, T_g , was defined by the intersection of the extrapolated straight line curves above and below the transition and the linear coefficients of thermal expansion were determined from the

gradients of these lines. The absolute accuracy of these latter values is estimated as about 5% but on a comparative basis the accuracy is rather better.²⁴

Specimens for adhesion testing were plaques (approximately $125 \times 75 \times 5$ mm) made by the use of a Netstal SM 60/40, ram type, 95 g capacity injection molding machine. A sample of cured rubber sheet, $125 \times 75 \times 1.75$ mm, was held in the mold with double sided adhesive tape and the PE (Hostalen G 7260 high density polyethylene from Hoechst Australia Ltd.) injected on to it, using a nozzle temperature of 200°C , an injection pressure of 4.0 MPa, dwell time 20 seconds and cooling time 30 seconds. No heating or cooling was supplied to the mold.

Adhesion was measured by peeling the rubber from the rigid PE at an angle of 90° , using an Instron model 1026, at a crosshead separation rate of 50 mm/min. Cuts were made through the rubber (but not the PE substrate) so that narrow strips (2–3 mm) were removed from between the 19 mm wide test strips to minimize the effect of a test on the adjacent strip. Use of a specially constructed trolley ensured that the peel angle remained close to 90° . Each specimen was turned through 180° after each test so that adjacent strips were peeled in opposite directions. At least three strips were measured (peeled length of each about 80 mm) for each rubber and an overall average value taken as the peel force.

RESULTS

Surface characterization of the rubber

The critical surface tension of wetting of a number of rubbers was determined as a means of characterizing the chemical nature of the surface. Although there was a certain amount of scatter in the results, little difference was apparent between the various rubber samples. The critical surface tension of wetting is about 25×10^{-3} N/m for all cases irrespective of whether or not the samples contained a paraffin wax and of the particular silica.

Thermal properties

A comparison was made of T_g and the linear coefficient of thermal expansion above and below T_g (β_L and β_g respectively) of the unreinforced rubber and rubbers containing the three silicas. Table II shows that the strongly reinforcing materials, Ultrasil VN3 and HiSil 233, have a significant influence on T_g and β_L , whereas the slightly reinforcing Neosyl Std. has a lesser effect. The coefficient of expansion below T_g is little affected by the silica type and loading.

TABLE II
Effect of silica type and loading on thermal properties of the rubber

Property	No silica	60 phr silica ^a			30 phr silica ^a		
		Ultrasil	Hi Sil	Neosyl	Ultrasil	Hi Sil	Neosyl
Glass transition temperature, T_g (°C)	-56	-64	-64	-62	-60	-60	-60
Coefficient of thermal expansion below T_g , β_g ($\times 10^4$ K ⁻¹)	1.0	0.7	0.7	0.7	0.8	0.7	0.7
Coefficient of thermal expansion above T_g , β_L ($\times 10^4$ K ⁻¹)	2.75	0.70	0.75	2.0	2.0	2.1	2.4

^a Formulations contained no wax.

Peel tests

Table III shows the average peel force for rubbers containing 30 and 60 parts per hundred parts of rubber, by weight (phr) of the three silicas. From the first line of the two upper sections it is seen that, 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.

Earlier work suggested²⁰ that the addition of small amounts (a few phr) of a paraffin wax, normally incorporated to improve sunlight resistance, had a beneficial effect on adhesion. Results for a series of rubbers, made to investigate this point, are also given in Table III but show no consistent effect. Paraffin wax in rubber normally migrates to the surface, but contact angle measurements show that it does not materially alter the critical surface tension of wetting of the surface. In one experiment, a small amount of melted paraffin wax was spread on the surface of a rubber which contained no wax, the wax allowed to solidify and the sample laminated to PE and tested. The peel strength was approximately 40% lower than the same rubber without the wax, which is an example of the weak boundary layer effect.

Since the various techniques used to examine the physical and chemical nature of the surface of these rubbers indicated no significant differences between them, explanation of the observed peel force range was sought in terms of the physical properties of these mixes. Values of these properties for representative mixes are given in Appendix 2. Figures 1-3 show that for a given silica loading the peel strength decreases with increasing 300% modulus, but increases with increasing tensile strength and elongation at break and also hardness (not illustrated).

TABLE III

Effect of silica type and loading and of the addition of a paraffin wax on the peel force

Amount of paraffin wax (phr)	Peel force ^a (N)		
	Ultrasil VN3	Hi Sil 233	Neosyl Std.
Silica loading 60 phr			
—	40	35	10
1	47	32	11
2	45	35	10
4	38	29	11
Silica loading 30 phr			
—	17	8	3
1	9	13	4
2	10	10	5
4	17	14	4
No silica 1 ^b			

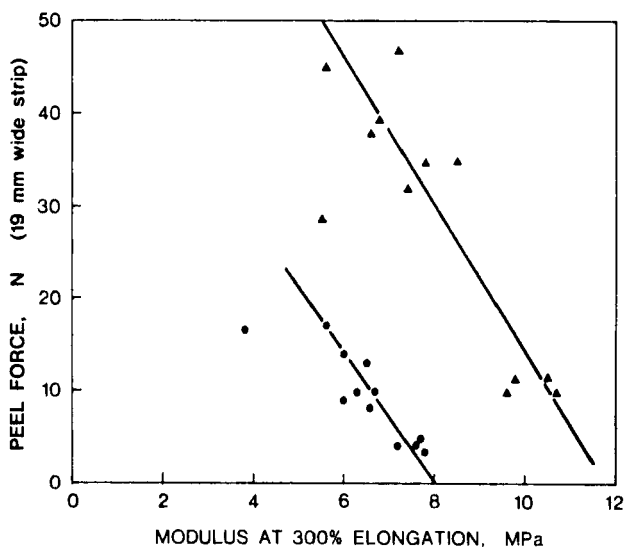
^a For strips 19 mm wide. Peel force accuracy in all cases approximately ± 1 N^b Effectively fell apart in the testing machine.

FIGURE 1 Relationship between peel force and modulus at 300% elongation of the rubber. ● 30 phr silica; ▲ 60 phr silica.

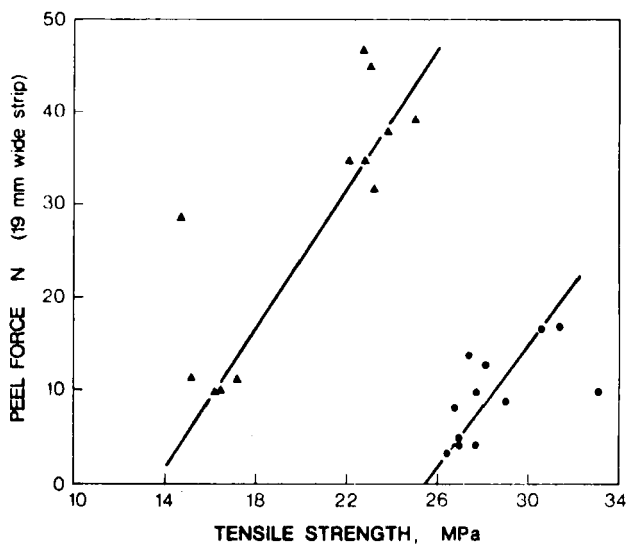


FIGURE 2 Relationship between peel force and tensile strength of the rubber. ● 30 phr silica; ▲ 60 phr silica.

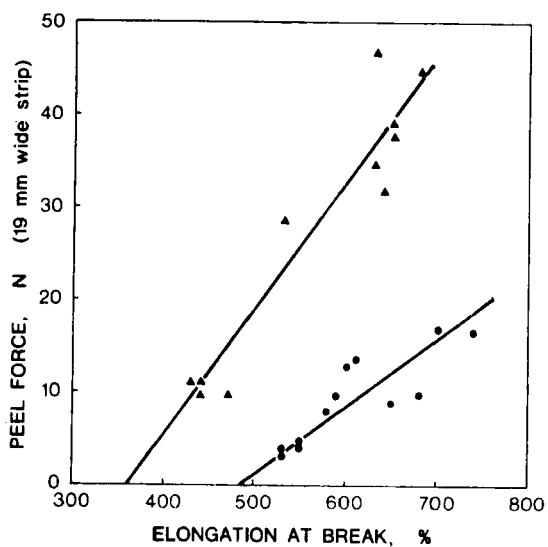


FIGURE 3 Relationship between peel force and elongation at break of the rubber. ● 30 phr silica; ▲ 60 phr silica.

DISCUSSION

The observed differences in peel force between the various systems cover a wide range. This is not simply a result of differences either in the physical or chemical nature of the surfaces of these systems. It was shown²¹ that textural differences, arising from deliberate roughening of the rubber surface prior to the injection of the PE, are not utilized 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 the 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 appeared smooth and glossy, it seems likely that penetration into the rubber surface did not occur.

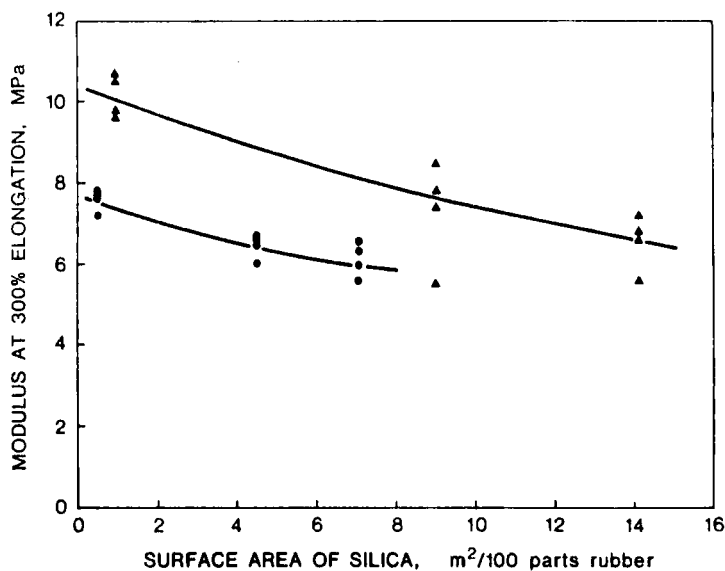


FIGURE 4 Relationship between peel force and the surface area of the silica. ● 30 phr silica; ▲ 60 phr silica.

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 adhesion strength is clearly discernible in the case of the paraffin wax applied to 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.

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

The data in Table III indicate that the peel force is related to the silica particle size. As Neosyl Std. has only mildly reinforcing abilities, it seems that the aggregates are not broken up during compounding and that consequently the BET method overestimates the surface area in contact with the rubber. The surface area has been calculated on the basis of an aggregate size of 1μ , which gives a value of about $1.5 \text{ m}^2/\text{g}$. While only very approximate, this enables the overall relationship between effective reinforcing agent surface area and other factors to be depicted (Figures 4 and 5). (The effect of silica type and loading on such bulk properties as modulus and tensile strength

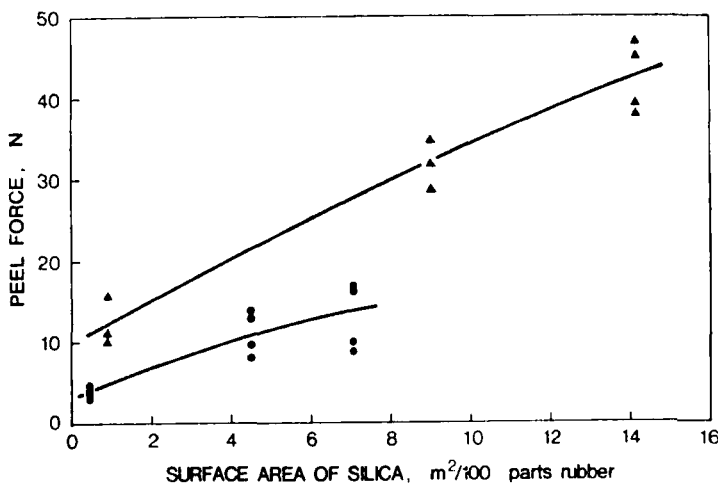


FIGURE 5 Relationship between the modulus at 300% elongation of the rubber and the surface area of the silica. ● 30 phr silica; ▲ 60 phr silica.

is in agreement with that normally found for white reinforcing agents²⁵). Thus, for a given silica loading the peel force in these systems is dependent on the silica particle size through the effect which the particle size has on the bulk physical properties of the rubber. The variation with silica loading indicates that other factors are also involved in determining the peel strength of these laminates.

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 (see Figure 6). Thus, there are differences in the effective test conditions, depending on the bulk physical properties of the rubber being peeled, which should be borne in mind when comparing the peel results of different systems.^{26, 27}

Thermal analysis showed that both T_g and the coefficient of thermal expansion in the rubbery state, β_L , were significantly changed by the presence of the silica (Table II). Little work has been reported on the effect of fillers on T_g and the coefficients of expansion of elastomers, but the available data, on systems containing carbon black, is quite at variance with the present results on silica reinforced rubber.²⁸

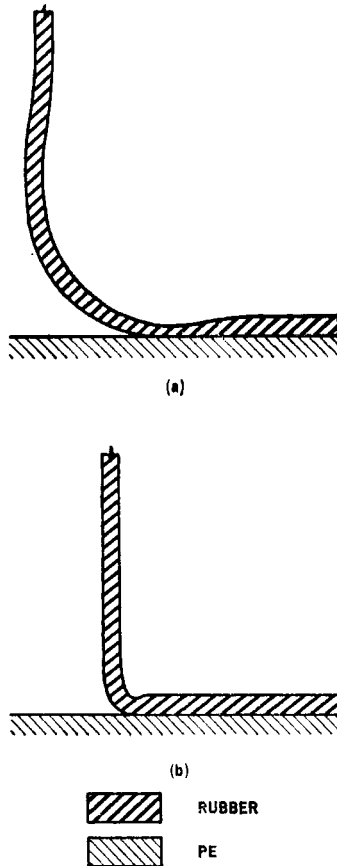


FIGURE 6 Schematic representation of a peel test. (a) stiff rubber at low loads; (b) stiff rubber at high loads and soft rubber at all loads.

With unreinforced systems, it has been reported¹⁶⁻¹⁹ 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 was that as T_g increases more energy is expended in viscoelastic deformations at the failure site.^{18, 19} At high cross link densities the question of

shrinkage stresses giving rise to a zone of high stress adjacent to the substrate, which could lead to a decrease in the observed peel force, must be considered.^{16, 29, 30}

In the present case, the largest decrease in T_g was shown by the rubbers with the larger amounts of the strongly reinforcing silicas, which were also the systems which showed the highest peel force. Also, there is a positive correlation between the coefficient of thermal expansion in the rubbery region, β_L , and the peel force such that the peel force is higher the smaller is

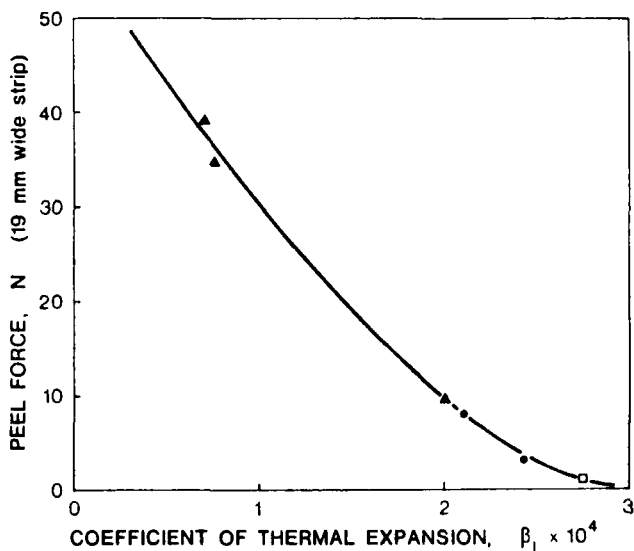


FIGURE 7 The peel force as a function of the coefficient of thermal expansion in the rubbery region of the rubber. ● 30 phr silica; ▲ 60 phr silica; □ no silica.

β_L (Figure 7). This is probably a manifestation of the effects of shrinkage stresses at the rubber-PE interface. As the peel test specimens were made by injecting the molten PE on to the rubber which was at room temperature, those rubbers with the smallest coefficient of thermal expansion evidently resulted in peel test specimens with smaller levels of frozen-in stresses at the interface, and this was a major contributing factor in the higher peel force displayed by these systems by comparison with the others.

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 in part from the effect of the silica particle size on bulk properties of the rubber, such as tensile strength and modulus. 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 molding. These interface stresses significantly modify the peel strength of the laminates. Surface chemical and surface roughness effects made little, if any, contribution to the adhesion strength of these systems.

Acknowledgements

The author wishes to thank Dr. B. C. Ennis for the thermal analyses and Mr. P. Dunn for helpful discussions on rubber formulating.

References

1. K. Allison, *Rubber World*, **158**, (1) 35 (1968).
2. Y. Iyengar, *Rubber World*, **148**, (9) 39 (1963).
3. J. R. Creasey and M. P. Wagner, *Rubber Age*, **100**, (10) 72 (1968).
4. J. R. Creasey, D. B. Russell and M. P. Wagner, *Rubb. Chem. Technol.* **41**, 1300 (1968).
5. N. L. Hewitt, *Rubber Age*, **104**, (1) 59 (1972).
6. Z. V. Shchichko, *Kauch. Rezina*, **26**, (7) 18 (1967).
7. V. A. Glagolev, *et al.*, *Sov. Rubb. Technol.* **30**, 31 (1971).
8. N. L. Hewitt and M. P. Wagner, *Adhesives Age*, **17**, (10) 35 (1974).
9. G. J. Crocker, *Rubb. Chem. Technol.* **42**, 30 (1969).
10. S. S. Voyutskii, *et al.* *Rubber Age*, **105**, (2) 37 (1973).
11. A. N. Gent and A. J. Kinloch, *J. Polym. Sci. A-2* **9**, 659 (1971).
12. E. H. Andrews and A. J. Kinloch, *Proc. Roy. Soc.* **A332**, 385 (1973).
13. E. H. Andrews and A. J. Kinloch, *Proc. Roy. Soc.* **A332**, 401 (1973).
14. E. H. Andrews and A. J. Kinloch, *J. Polym. Sci. Symp.* **46**, 1 (1974).
15. A. N. Gent, *J. Polym. Sci. A-2* **9**, 283 (1971).
16. V. G. Raevskii and S. S. Voyutskii, *Rubb. Chem. Technol.* **34**, 879 (1961).
17. E. A. Kogan *et al.*, *Colloid J. USSR* **32**, 310 (1970).
18. K. Kendall, *J. Polym. Sci., Polym. Phys. Ed.* **12**, 295 (1974).
19. E. H. Andrews and A. J. Kinloch, *J. Polym. Sci. Polym. Phys. Ed.* **11**, 269 (1973).
20. J. M. Woodford, unpublished results.
21. C. E. M. Morris, Tech. Rept. No. 667 "The Adhesion of Silica Reinforced Natural Rubber to Polyethylene", Materials Research Laboratories, Melbourne (1976).
22. J. W. Sellers and F. E. Tooner, in *Reinforcement of Elastomers*, G. Kraus ed. (Interscience, New York 1965), pp. 405-424.
23. Joseph Crossfield and Sons Ltd., Neosyl Brand Silica Data Sheet (1971).
24. R. Gaskill and E. M. Barrall, *Thermochim. Acta*, **12**, 102 (1975).
25. H. Westlinning and H. Fleischhauser, in *Reinforcement of Elastomers*, G. Kraus ed. (Interscience, New York, 1965), pp. 425-490.
26. P. B. Lindley, *J. Instn. Rubber Industr.* **5**, 243 (1971).
27. A. N. Gent and G. R. Hamed, *J. Adhesion*, **7**, 91 (1975).
28. G. Kraus, *Adv. Polym. Sci.* **8**, 155 (1971).
29. K. Kendall, *J. Phys. D., Appl. Phys.* **6**, 1782 (1973).
30. K. Kendall, *ibid.* **8**, 1722 (1975).

APPENDIX 1

Trade name and chemical composition of compounding ingredients^a

Compound	Trade name	Manufacturer
Hydrated silica	Ultrasil VN3	Füllstoffgesellschaft mbH
Hydrated silica	Hi Sil 233	Pittsburgh Plate Glass Co.
Hydrated silica	Neosyl Std.	Joseph Crossfield and Sons Ltd.
Tetramethyl-thiuram-disulfide	Vulcafor TMT	Imperial Chemical Industries Ltd.
N-cyclohexyl-2-benzthiazyl-sulfenamide	Vulcafor HBS	Imperial Chemical Industries Ltd.
Poly(ethylene glycol)	Carbowax 4000	Union Carbide Aust. Ltd.
Paraffin wax	Heliozone wax	E.I. du Pont de Nemours

^a These particular materials were used because they were readily available. No significance should be ascribed to their use in place of similar products of other manufacturers.

APPENDIX 2

Composition and physical properties of representative formulations

Formulation no. Additional ingredients (phr)	1 Basic formulation ^{a, b}	2	3 ^c	6	9 ^e	10 ^e	
Silica, Ultrasil VN3		60	60	30	30		
Hi Sil 233						60	
Neosyl Std.							
Poly(ethylene glycol)		1.2	1.2	0.6	0.6	1.2	
Paraffin wax			4		4		
Modulus at 300% (MPa)	3.9	6.8	6.6	3.8	5.6	8.5	
Tensile strength (MPa)	24.8	25.0	23.8	30.6	31.4	22.8	
Elongation at break (%)	470	650	650	740	700	630	
Hardness (IRHD)	47	92	90	66	65	83	
Formulation no.	13 ^c	14 ^c	17 ^c	18 ^c	21 ^c	22 ^c	25 ^c
Silica, Ultrasil VN3							
Hi Sil 233	60	30	30				
Neosyl Std.				60	60	30	30
Poly(ethylene glycol)	1.2	0.6	0.6	1.2	1.2	0.6	0.6
Paraffin wax	4		4		4		4
Modulus at 300% (MPa)	5.5	6.6	6.0	10.7	10.5	7.8	7.2
Tensile strength (MPa)	14.7	26.8	27.4	16.2	17.2	26.4	27.7
Elongation at break (%)	530	580	610	440	440	530	550
Hardness (IRHD)	86	72	63	77	72	58	57

^a Basic formulation: SMR 5 100, zinc oxide 3, stearic acid 2, tetramethylthiuram-disulfide 1.5, N-cyclohexyl-2-benzthiazyl-sulfenamide 0.5, sulfur 1.5.

^b Formulation no. 1 also contained 1.5 phr phenyl- β -naphthylamine not included in any other formulation.

^c SMR 5L in place of SMR 5.