Effect of the Molecular Length of n-Alkylsilanes on the Adhesion at a Rubber/Glass Interface

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The effect on the peeling energy, G, of glass/styrene-butadiene rubber (SBR) assemblies of the length, N, of the alkyl chain, ranging from 4 to 30 carbon atoms, of silane coupling agents is determined. Experimentally, it is shown that G strongly increases with N. Therefore, considering that the rheological model of adhesion (or model of multiplying factors) is valid, G is assumed equal to the product of three terms: the reversible adhesion energy, W, at the interface, the viscoelastic dissipation factor, Φ, of SBR and a "molecular factor" to be determined. Finally, it appears that this latter factor depends linearly on N. Such a result should be consistent with an extraction ("suction") process of the silane alkyl links from bulk SBR during peeling experiments.

KEY WORDS rubber-glass interfaces; peeling energy; reversible work of adhesion; viscoelastic losses; molecular length of coupling agents; SBR; molecular extraction.

1. INTRODUCTION

The adhesion mechanisms at rubber-glass interfaces are generally complex. Different types of interactions, in particular chemical or physico-chemical interactions, can be involved and, thus, it is difficult to perform a precise mechanical analysis of the forces required to break such assemblies. The use of coupling agents, such as silanes for example, can increase the failure strength of these interfaces. This increase is due to either the establishment of covalent bonds between the glass and the elastomer in the case of di-functional silanes, which are able to react at their both ends, or to the diffusion into the bulk elastomer of the non-reacting chain in the case of mono-functional silanes (chemical reaction at the glass surface only). In both cases, it is conceivable that the molecular length, or "coupling length," of the coupling agent could play a major role in determining the interfacial adhesive strength.

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The aim of the present study is to determine the influence on the peeling energy, G, of glass/styrene-butadiene rubber (SBR) assemblies of the alkyl chain length N, defined as the number of carbon atoms in the chain, of monochlorosilane coupling agents.

2. EXPERIMENTAL

Glass plates (Saint-Gobain), with a thickness of 3 mm, have been used as received or after having been subjected to an alkali-extraction treatment, since a recent study[1] has clearly shown that alkali ions behave as poisons for the adhesion between polymer and glass. Prior to grafting of silanes, these plates have been washed with distilled water, then absolute ethanol and, finally, dried at 200°C.

A series of n-alkyl-dimethyl chlorosilanes (Petrarch Systems) of general formula:

$$Cl—(CH_3)_2Si—(CH_2)_{N-1}—CH_3,$$
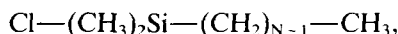
with alkyl chain length N equal to 4, 10, 18 or 30 carbon atoms, have been employed. These silanes are grafted onto untreated and alkali-extracted glass plates by dipping these plates for 4 hrs in 2% silane solutions in ethanol. The plates are then carefully washed at the boiling temperature of ethanol for 24 hrs, dried under vacuum and stored in a dessicator. After grafting, glass surfaces are analysed by Fourier transform infrared (FTIR) and X-ray photoelectron (XPS) spectrometries, in order to determine the areal density, v, of grafted silanes. The surface energy, γ, defined as the sum of its dispersive γ^D and polar γ^P components, of glass plates as well as SBR sheets are determined by contact angle measurements of drops of the usual liquids. This is performed on SBR by means of the single-liquid-phase method (α-bromonaphthalene, tricresylphosphate and water) and no hysteresis phenomenon (difference between advancing and receding angles) is evidenced. For glass plates, the two-liquid-phase method[2] (drops of water onto glass plates immersed in different n-alkanes) is employed. With such a method, contrary to classical wetting measurements, hysteresis phenomena are greatly reduced and can be considered as negligible to a first approximation. For SBR, the following values of $\gamma_{SBR} = 41$, $\gamma_{SBR}^D = 39.5$ and $\gamma_{SBR}^P = 1.5$ mJ/m^2 are obtained. Since the polar component of the surface energy of SBR is very low, it can be considered that this elastomer is not able to establish with glass surfaces strong non-dispersive interactions, such as acid-base interactions, for example. Therefore, to a first approximation, the reversible energy of adhesion, W, between glass plates and SBR is estimated in all cases by means of the following relationship[3,4]:

$$W = 2(\gamma_{glass}^D \cdot \gamma_{SBR}^D)^{1/2} + 2(\gamma_{glass}^P \cdot \gamma_{SBR}^P)^{1/2} \qquad (1)$$

Only one type of SBR (BASF 1500), with a styrene content of 23.5% by weight, is used. Assemblies are obtained by moulding at 150°C for 2 hrs. During this operation, the SBR is slightly crosslinked by means of 0.45% by weight of dicumylperoxide. A backing (cotton fabric) is incorporated on the external side of SBR to reduce its elongation during peeling.

The fracture energy, G, of the resulting assemblies is measured by 180° peeling experiments on samples of width b = 2.5 cm, by means of a tensile testing machine (Lhomargy DY22). Measurements are performed at room temperature and at cross-head speeds, v, ranging from 0.5 to 250 mm/min for untreated glass plates and from 0.5 to 50 mm/min for alkali-extracted glass plates, too-large values of G being obtained in this latter case for v higher than 50 mm/min. Under these conditions, G is related to the peeling force, F, by the relation:

$$G = 2F/b \qquad (2)$$

3. RESULTS AND DISCUSSION

It is first shown that the fracture energy, G, of the assemblies greatly increases with either the length, N, of the alkyl chain, or the peeling rate, v (Figure 1 a & b for un-treated and alkali-extracted glass plates, respectively).

In logarithmic scales, G increases linearly with v (Figure 2 a & b). Therefore, as for many other systems, G can be expressed as a power function of the peeling rate, v, according to:

$$G = \beta \cdot v^{\alpha} \qquad (3)$$

Equation (3) can be interestingly compared with the rheological model of adhesion, originally proposed by Gent and Schultz[5], i.e.:

$$G = G_O \cdot \Phi(v,T) \qquad (4)$$

where G_O is the intrinsic adhesion energy of the interface and Φ is the viscoelastic dissipation function of the elastomer which depends on the cross-head speed, v, and the temperature, T, at which the peeling experiment is performed. Therefore, to a first approximation, the term v^{α} can be considered equal to the function Φ. The variations of the exponent, α, versus the alkyl chain length, N, are given in Figure 3 for both types of glass plates used. It appears that α slightly increases with N in the case of alkali-extracted glass. On the contrary, for untreated glass plates, α first increases and then slightly decreases with N. Such variations indicate that the hysteritic losses during peeling experiments are modified by the presence and the molecular length of grafted silanes. Nevertheless, the amplitude of this modification appears to be small and, to a first approximation, it can be considered that the exponent α is almost kept constant whatever N (only average values of α, i.e. 0.17 and 0.32 for untreated and alkali-extracted glasses, respectively, are thus taken into account). Consequently, both of the terms Φ and v^{α} can be considered independent of N, indicating that, to a first approximation, the hysteritic losses during peeling experiments stem mainly from the bulk SBR rather than from the interfacial region. Therefore, equation (3) allows us to define the parameter, β, equal to G_O, which depends only on the physico-chemical interactions established at the interface between glass and SBR and, in particular, only those depending on the reversible adhesion energy, W, the areal density of grafted silanes, ν, and the alkyl chain length, N.
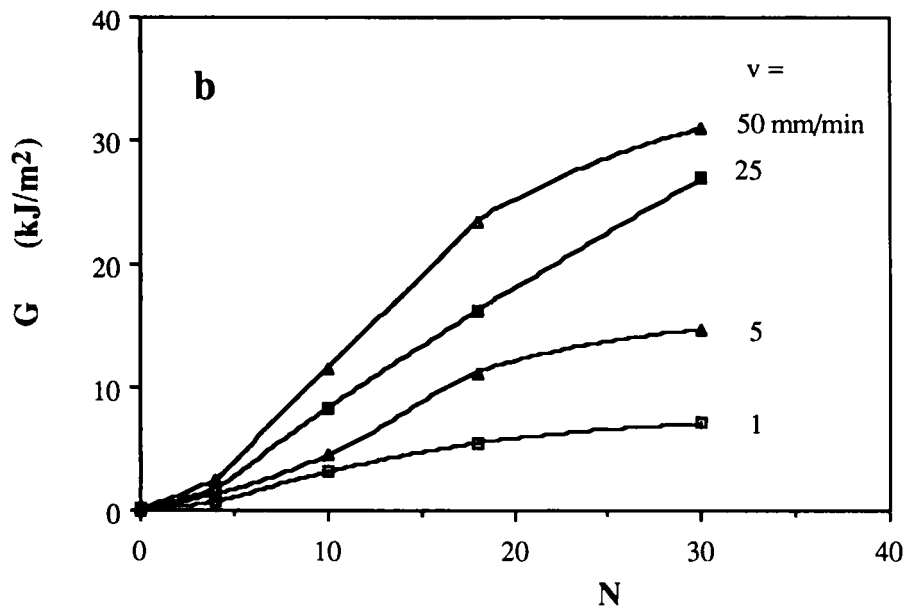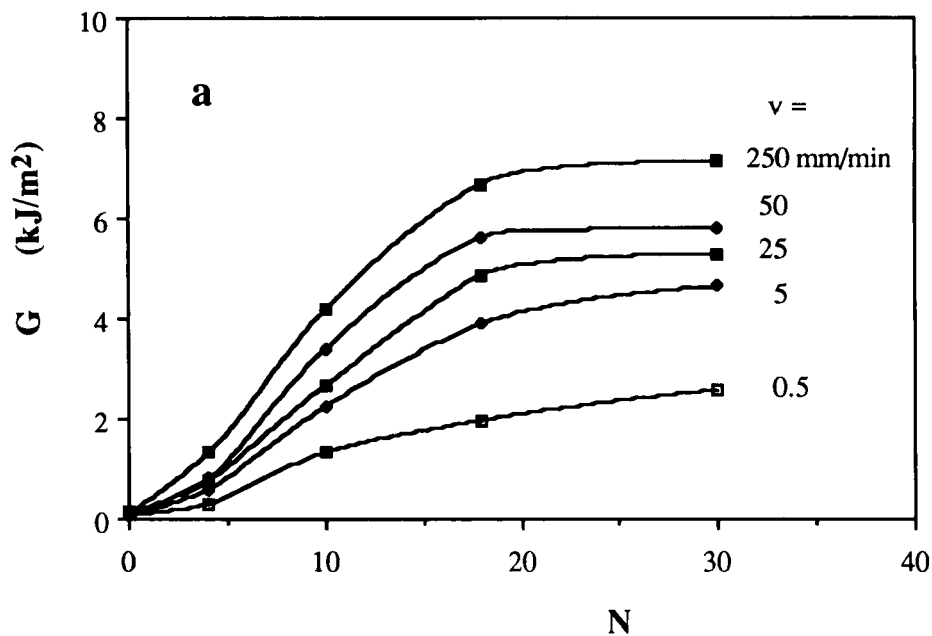
GURE 1   Peeling energy, G, *versus* N at different peeling rates, v: a) untreated glass; b) alkali-tracted glass.
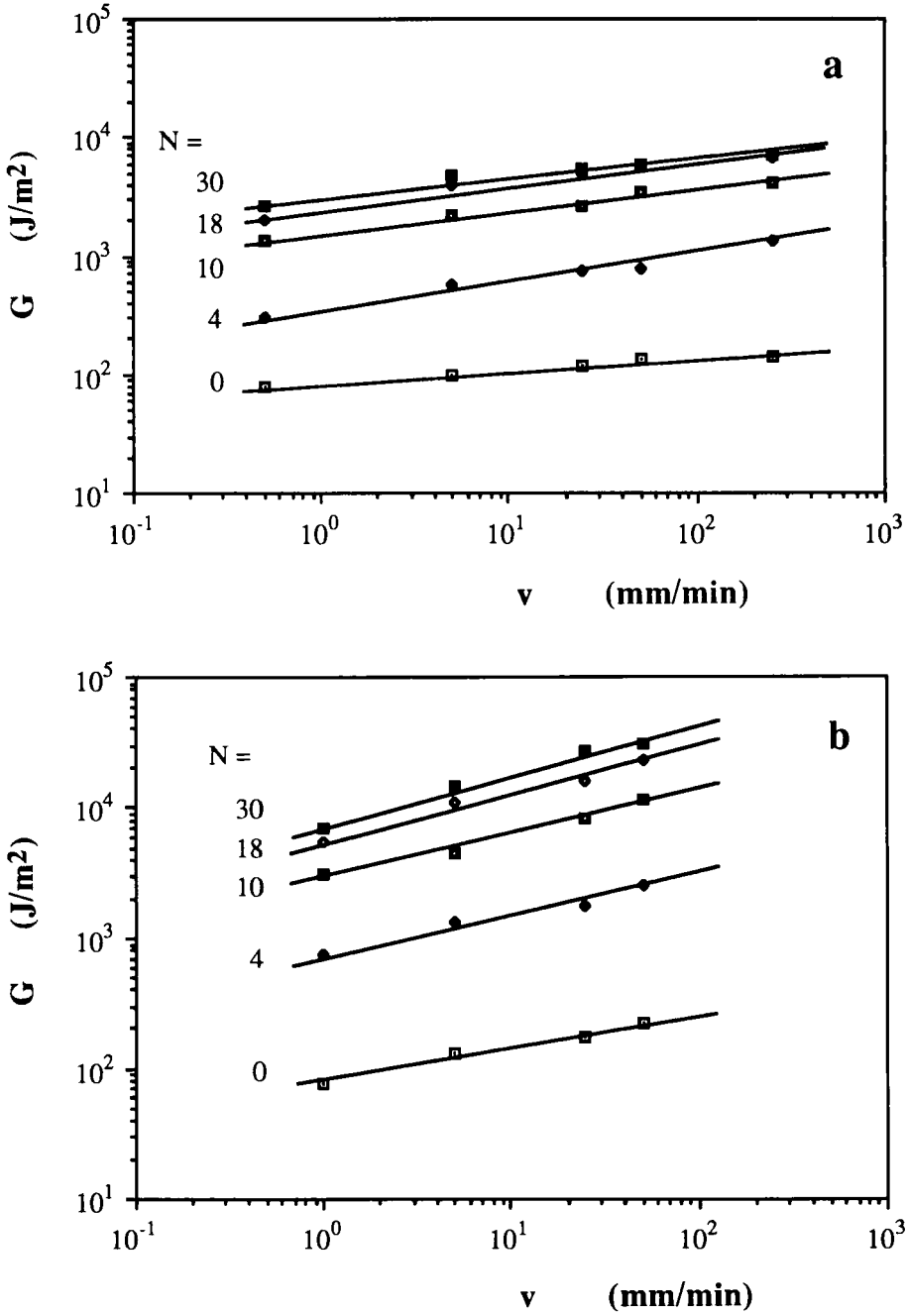
FIGURE 2   Peeling energy, G, *versus* peeling rate, v, in logarithmic scales for different values of N: a) untreated glass; b) alkali-extracted glass.
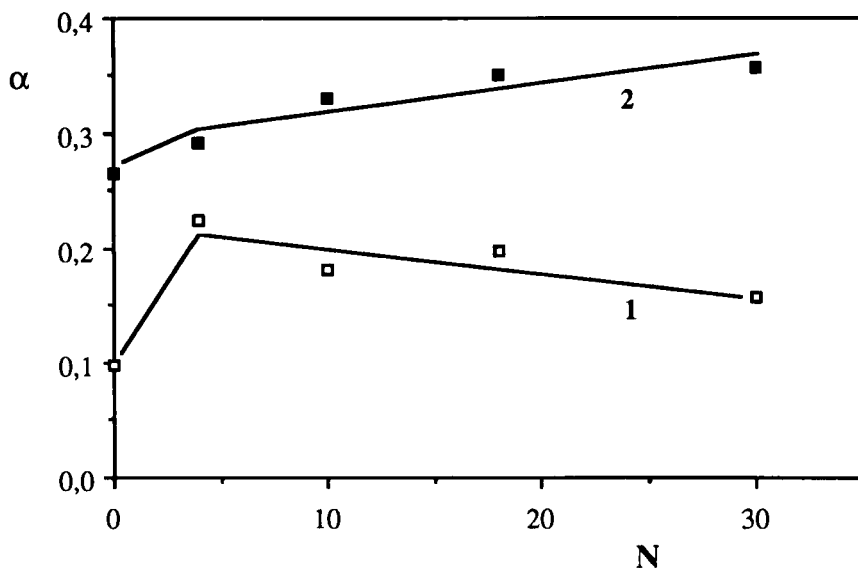
FIGURE 3   Variation of the exponent α of the peeling rate (equation (3)) *versus* N for untreated (1) and alkali-extracted (2) glasses.

Before attempting the analysis of the dependence of G_0 on the work of adhesion, it is first necessary to examine the variation of the total surface energy, γ_{glass}, of glass plates as a function of N (Figure 4). Similar results are obtained for both types of glass used. For values of N less than about 10, a linear decrease of γ_{glass} *versus* N is first observed. This straight line can be extrapolated to the expected value of the surface energy of a plate totally covered by alkyl chains, in other words corresponding to a polyethylene (PE) surface, *i.e.* about 35 mJ/m^2.[6] Therefore, it appears that for N$\approx$16, the glass surface should be totally hidden by the alkyl chains. Remembering that the mean surface area of a methylene group, CH_2, is equal[7] to about 0.06 nm^2, such a value of N corresponds perfectly to the areal density of CH_2 groups per nm^2 for a monolayer of close-packed hydrocarbon chains (crystal-like structure)[7,8] lying on the surface. As a consequence, in the range of N-values considered, the areal density, v, of grafted silanes can be estimated to be equal to about 1/nm^2. Such a density is low and equal to about half that measured on silica surfaces[9] in the case of an esterification of superficial silanol groups by a series of n-alcohols, for example.

Figure 4 also shows that γ_{glass} suddenly increases in the range of N-values from 10 to 18, then decreases again linearly to reach the surface energy of PE at N$\approx$35–40. First, a sudden change of the grafting ratio for N between 10 and 18 can be rejected, a previous study on silica surfaces[9] having shown that this ratio is only slightly affected by the chain length of the grafted molecules. However, when the chain length is increased, a steric hindrance phenomenon occurs and, thus, a structural transition of the arrangement of hydrocarbon chains near the glass surface, at constant areal density of grafting, can be invoked, in agreement with a recent
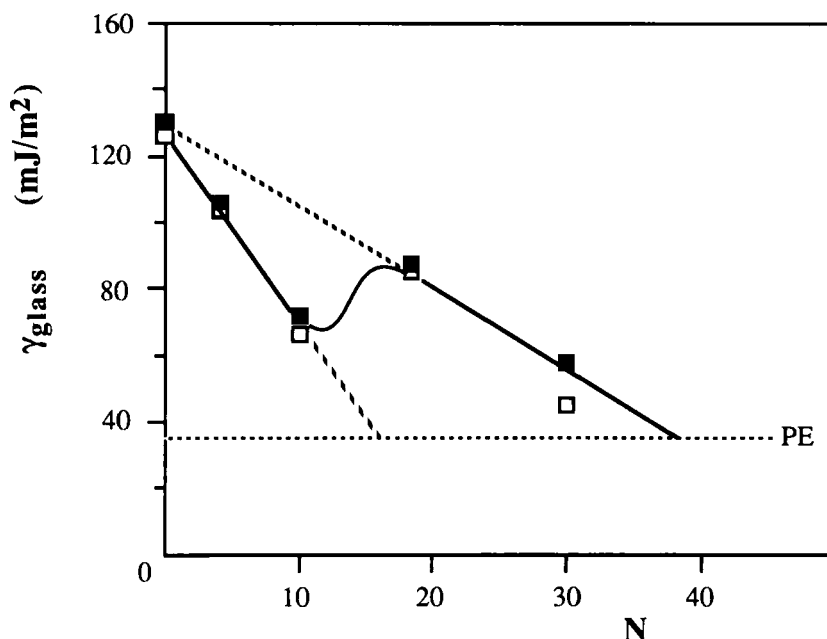
FIGURE 4 Surface energy, γ_{glass}, of glass surfaces *versus* N for untreated ($\square$) and alkali-extracted ($\blacksquare$) glasses.

work.[10] Therefore, a non-complete bilayer, and perhaps a trilayer, of alkyl chains in a crystal-like structure could be formed on the glass surface. The existence of such thick layers could explain the value of N of about 40 corresponding to the total coverage (surface energy of PE) of the glass surface by hydrocarbon chains, since 40 corresponds to the average value between N = 32 for a dense bilayer and N = 48 for a dense trilayer[10] for the same areal density, v. It is worth noting that similar conclusions can be drawn from the variations *versus* N of either dispersive or polar components of the surface energy of glass plates.

Finally, it can be concluded that, to a first approximation, the areal density, v, of grafted silanes on both types of glass surfaces is constant whatever the alkyl chain length and equal to about one chain per nm^2. Unfortunately, it was impossible to confirm this estimated value of v either by FTIR or by XPS, mainly due to the fact of a lack of sensitivity for the former technique and of a hydrocarbon contamination, always involved in both types of glasses, for the latter technique. Only the presence of the silane of N = 30 is unambiguously observed by XPS. However, such results confirm that the grafting ratio of the given silanes on glass surfaces is low.

If the reversible work of adhesion is now considered, it appears that G_O increases (Figure 1), while W decreases (Table I) with the length N. This fact indicates that the alkyl chains have certainly "dissolved" into bulk SBR, otherwise both the variations of G_O and W *versus* N would have been similar.

Therefore, two phenomena, which could occur during peeling experiments, can be invoked: first an extraction process, called a "suction" process,[11] of the alkyl

TABLE I

Reversible work of adhesion, W, between SBR
and untreated or alkali-extracted glasses
as a function of N

N	W (mJ/m^2)	
	Untreated	Alkali-extracted
0	136	139
4	128	129
10	103	108
18	119	119
30	84	96

chains from the SBR network and secondly, a chain scission process[12] in the case where the alkyl chains would have reacted chemically (co-crosslinking) with the SBR network in the presence of peroxide. The magnitude of the former phenomenon is related to the product νN, whereas that of the latter varies as the square of ν. In both cases, the areal density ν of grafted silanes must play a major role, but can be considered constant in our case, as previously stated. However, since the glass surface is not totally hidden by the presence of silanes (Figure 4), it is conceivable that W is an important factor affecting the value of G_O.

According to the rheological model of adhesion (Ref. 5 and equation (4)) and considering, in a first step, that a suction phenomenon is involved, G_O can be considered equal to:

$$G_O = W \cdot \nu N \qquad (5)$$

Figure 5 clearly shows that the quantity G_O/W is indeed proportional to N for both systems studied. According to equation (5), such a result suggests that a co-crosslinking reaction between silanes and SBR by means of the peroxide has not taken place and that a suction process of the alkyl chains from the SBR network during peeling is the most likely. Moreover, a fracture phenomenon of these alkyl chains during extraction can be rejected at the temperature and peeling rates used in this study. Nevertheless, it is worth mentioning that, in all cases, the failure is apparently adhesive. However, contact angles of drops of water onto glass surfaces measured after peeling are higher than those obtained on initial glasses, even for non-grafted glasses. Since this phenomenon also occurs for untreated glasses, for which peeling energy is very low, it could be attributed either to decomposition products of the peroxide or even to the presence of SBR chains (maybe the smallest chains), which are not linked to the SBR network near the interface. Therefore, this observation is not in fundamental contradiction with a suction process of the silane alkyl chains.

The slope of the variation of G_O/W versus N for alkali-extracted glass is about twice that corresponding to untreated glass (Figure 5). This could be attributed, to a first approximation, to the presence of alkali ions, which are known to be poisons for adhesion,[1] at a higher concentration near the glass surface in the latter case. The same assumption can also be invoked to explain the different values of the exponent
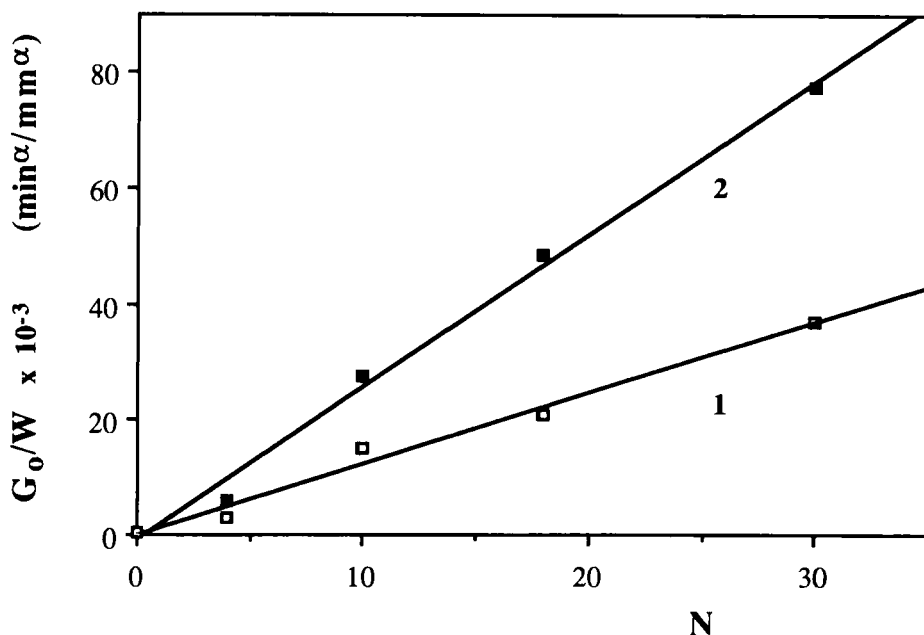
FIGURE 5   Variation of the ratio, G_O/W, *versus* N for untreated (1) and alkali-extracted (2) glasses.

α (equation (3)) and, consequently, of the hysteritic losses during peeling experiments, as previously observed.

Finally, the peeling energy, G, could be expressed as:

$$G \equiv W \cdot \nu N \cdot \Phi \qquad (6)$$

Therefore, in this relationship, the product νN could be considered as a "molecular dissipation factor," as previously proposed by Carré and Schultz,[13] here related to the suction phenomenon. Such a parameter allows us to explain the fact that, when the viscoelastic dissipation function Φ tends toward unity, *i.e.* either at high temperature or at very low peeling rate, the fracture energy, G, is much larger (100 to 1000 times) than the reversible work of adhesion, W.

4. CONCLUSION

The present study deals with the influence of the alkyl chain length of silane coupling agents on the peel strength of glass-styrene butadiene rubber assemblies. It is shown that an extraction phenomenon ("suction process")[11] of these chains from the bulk SBR can be invoked to explain the values of the peeling energy, G, of such assemblies. To a first approximation, G can be expressed as:

$$G \equiv W \cdot \nu N \cdot \Phi$$

In this relationship, the product νN plays the role of a "molecular dissipation

factor,"[13] here related to the suction phenomenon, and allows us to explain why the intrinsic adhesive strength, G_O, is greatly higher than the reversible work of adhesion, W, between glass and SBR. Finally, since the areal density, ν, of grafted silanes has not been precisely determined, labelled silanes, such as perfluorosilanes, could be used to quantify ν by XPS in future work, in order to define more precisely the influence of ν on G.

Acknowledgements

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