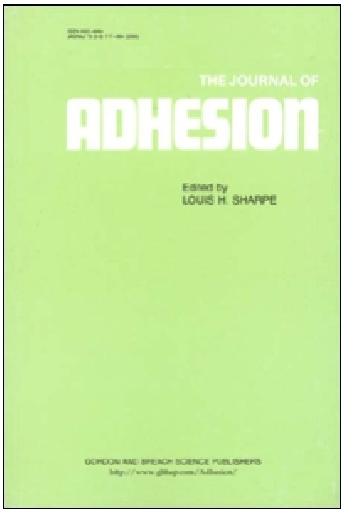

The Journal of Adhesion
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713453635

The Effect of Water on Matrix/Filler Adhesion in a Polyurethane Elastomer

M. R. Bowditch[a]; K. J. Stannard[a]
[a] Admiralty Research Establishment, Poole, Dorset, U.K.

To cite this Article Bowditch, M. R. and Stannard, K. J.(1987) 'The Effect of Water on Matrix/Filler Adhesion in a Polyurethane Elastomer', The Journal of Adhesion, 21: 3, 329 — 341
To link to this Article: DOI: 10.1080/00218468708074979
URL: http://dx.doi.org/10.1080/00218468708074979

J. Adhesion, 1987, Vol. 21, pp. 329–341
Photocopying permitted by license only

Printed in the United Kingdom

The Effect of Water on Matrix/Filler Adhesion in a Polyurethane Elastomer†

M. R. BOWDITCH and K. J. STANNARD

Admiralty Research Establishment, Holton Heath, Poole, Dorset BH16 6JU, U.K.

(Received July 24, 1986)

The static "moduli," failure stresses and dynamic moduli of both filled and unfilled polyurethanes were measured over a range of equilibrium water contents and these results are compared with those obtained from dry controls. Where barium sulphate was employed as the major filler component, it is shown that the presence of as little as ~0.7% water results in a profound degradation of mechanical properties with the loss of most of the contribution attributable to the presence of fillers as a result of hydrolytic disruption of filler/matrix adhesion. A quantitative relationship between water content and mechanical properties is established and the mechanics of the water/polymer/filler interaction are considered. Less dramatic effects were observed when barium sulphate was replaced by iron oxide and these were apparently further reduced by the use of a silane coupling agent.

KEY WORDS Failure stress; matrix/filler adhesion; mechanical properties; polyurethane elastomer; silane coupling agent, water absorption.

INTRODUCTION

The rubber investigated was a polyether-based polyurethane system, cured with a polymeric 4,4′-diisocyanatodiphenylmethane cross-linked with trimethylol propane and filled with barytes (and small amounts of fumed silica and carbon black) or iron oxide.

---

† Presented at the Tenth Annual Meeting of The Adhesion Society, Inc., Williamsburg, Virginia, U.S.A., February 22–27, 1987.

This material was of interest because of its acoustical properties. In certain applications such materials are required to possess a high attenuation and to match closely the sound propagating medium; in this case water. The impedance (z) of a material is a function of density (ρ) and velocity of sound within the material (c) as follows:

$$z = \rho \cdot c$$

It is often necessary to incorporate air in such materials to facilitate the shear deformations associated with high energy absorption. However, the inclusion of air leads to the reduction of c from typically $1500\,\mathrm{m\,s^{-1}}$ to lower values and, in order to re-establish matching, high density fillers, such as barytes or iron oxide are commonly used. In this work only air-free material has been investigated.

EXPERIMENTAL

Dumbells and other test pieces were cut from material sliced to about 1 mm thickness from cast sheet.

Low equilibrium water contents, up to about 1% w/w, were obtained by exposing material to environments of known relative humidity over saturated salt solutions. Higher values were achieved by immersing specimens in salt solutions and in distilled water. Equilibrium conditions were assumed to be established when specimens, equal in thickness to the prepared test pieces, failed to increase in mass after further exposure to the experimental environment.

Static "moduli" (at 20% extension) and failure stresses were measured using an Instron 1185 tensometer linked to a Hewlett Packard 85 computer. Six replicates were evaluated in each case and mean values are reported. Dynamic moduli were measured using a Polymer Labs Dynamic Mechanical Thermal Analyser (DMTA) machine, generally at 10 Hz. Surface area determinations were carried out using a Micromeritics 2200 high speed surface area analyser. Chemical analyses were undertaken with the use of a Varian AA 775 atomic absorption spectrometer and by classical qualitative methods.

Diffusion coefficients were measured on thin films, typically

0.5 mm thick. These films were immersed in distilled water at 20°C from which they were removed at intervals, mopped superficially dry and weighed before being returned to the water. Plots of percentage mass increase against root time in hours were prepared and diffusion coefficients were calculated[1] from the relationship:

$$D = \left(\frac{\text{slope} \times l}{m_\infty}\right)^2 \times 5.45 \times 10^{-11}\,\mathrm{m^2\,s^{-1}}$$

where D is the diffusion coefficient, slope is the initial linear slope of the water uptake *vs* root time plot, l is the thickness of the specimen in mm and m_∞ is the solubility of water in the material expressed as a percentage.

RESULTS AND DISCUSSION

"Modulus" values for both barytes-filled and unfilled material were obtained at various equilibrium water concentrations and plots of these results against water content are given in Figure 1. At the same time, failure stress results were also generated and these are presented in Figure 2. These figures show clearly the dramatic effect

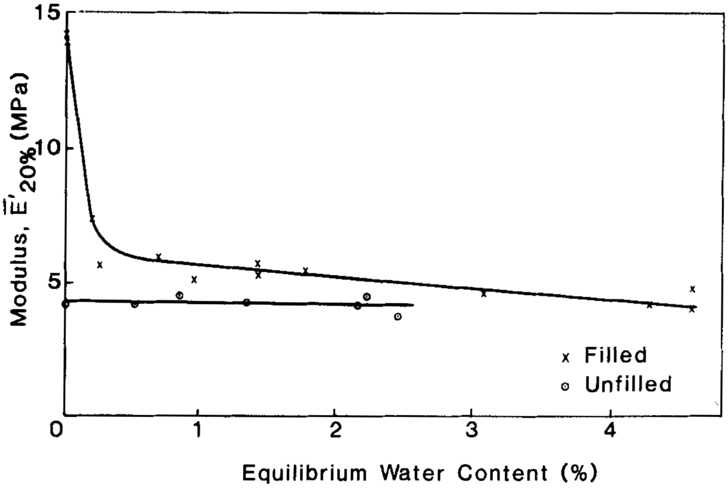

FIGURE 1 The effect of water on "modulus" of both filled and unfilled polyurethane.

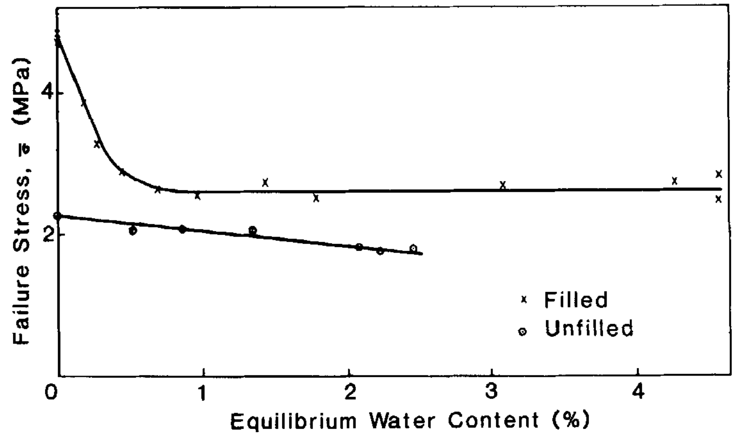

FIGURE 2 The effect of water on the failure stress of both filled and unfilled polyurethane.

on the mechanical properties of the filled material which result from the presence of quite low water contents. The presence of an equilibrium water content of about 0.7% leads to the almost total loss of the reinforcing effect of the filler.

Specific surface area determinations on the fillers used indicated that the silica was by far the most finely divided material with a value of 113.7 $m^2 g^{-1}$ whilst the relatively coarse lampblack had a surface area of ~20 $m^2 g^{-1}$. Barytes, had a surface area of only 0.31 $m^2 g^{-1}$. On the assumption[2] that each water molecule occupies $1.56 \times 10^{-18} m^2$ it was calculated that as little as 230 ppm water would be sufficient for a monomolecular layer over the entire surface of the fillers. In fact some twenty-six times this concentration appears to be necessary to destroy the fillers' contribution to modulus and to failure stress.

However, tests thus far had been conducted on specimens as soon as equilibrium conditions had been achieved and therefore, in case this had allowed insufficient time, at lower water concentrations, for degradation to occur, specimens containing 0.28% equilibrium water concentration were withdrawn and tested at intervals with the results given in Figure 3. These results suggest that the degradation rate-determining stage is complete by the time equilibrium is established. The 0.28% equilibrium water content was chosen

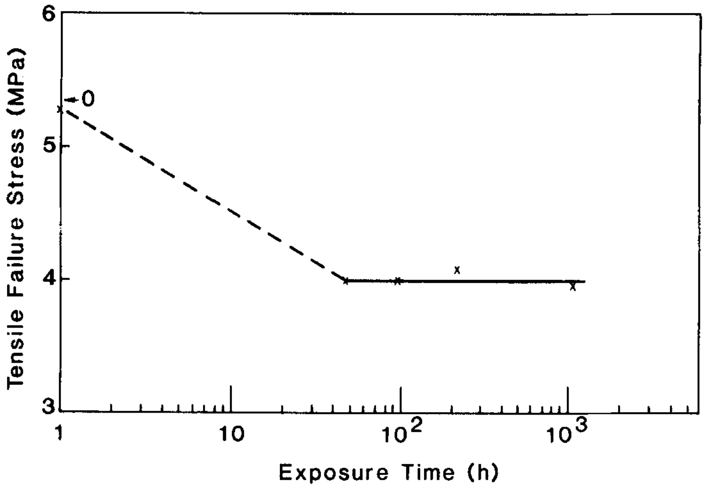

FIGURE 3 The effect of time on the degradative influence of moisture (0.28%) on a barytes-filled polyurethane.

because, although it had been shown to be insufficient to cause a complete loss of properties under the initial conditions of test, there was nevertheless more than enough to provide the few molecular layers which would presumably be sufficient to cause total disruption of polymer/filler adhesion.

In an attempt to clarify further the ultimate destination of absorbed water, water take-up experiments were carried out at two water activity levels with rubbers containing a range of barytes concentrations from 0 to ~65% w/w. The results are shown in Figure 4 where equilibrium water concentration is plotted against the polymer content of the various mixes. Values for equilibrium water contents for these formulations were also calculated on the assumption that the amount of water absorbed was a function of the polymer content only and was quite independent of the filler component. The theoretical curves are drawn on the figure and it can be seen that the experimentally determined points fall quite close to them. It is inferred from these results that, at these lower levels, water concentrates in the polymer, presumably at hydrogen bondable sites, rather than at the polymer/filler interface.

Samples of polyurethane rubber containing barytes filler alone

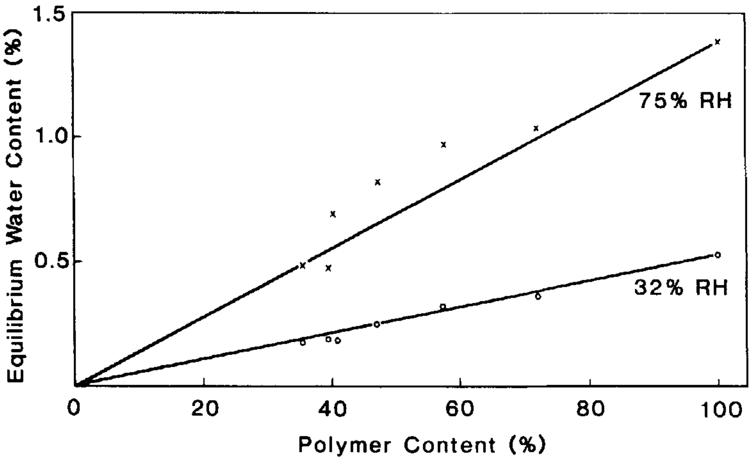

FIGURE 4 Equilibrium water content versus polymer content in a series of filled polyurethanes at two water vapour concentrations.

were made up, as were samples containing carbon black only and fumed silica alone. Initial, control static modulus values for these three formulations were obtained and similar modulus values were measured on specimens which had reached equilibrium in various humid environments. All these results, together with those obtained for the complete formulation, appear in Figure 5 where it can be seen that, of the three fillers, the barytes, which is present in the greatest abundance, contributes most to the superior properties of the original, filled composition. It can also be seen that it is this barytes-containing mix which is most seriously affected by the presence of absorbed water. At an equilibrium water content of about 0.6% it is evident that all those properties attributable to the presence of the barytes have been lost.

A curve obtained for the determination of the diffusion coefficient for the unfilled urethane is given as Figure 6 where it may be seen that the limit of solubility for water in the polymer is ~2.16%. This value is equivalent to the presence of ~0.9% in the filled product and so, by reference to Figure 5, it can be seen that the loss of properties attributable to the presence of fillers occurs well before the polymer itself is saturated with water. The diffusion coefficient of $1.51 \times 10^{-11}\ m^2\ s^{-1}$ is typical for such polyurethane formulations.

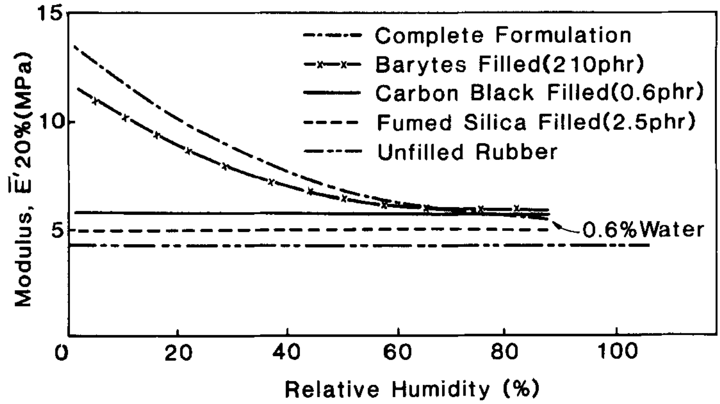

FIGURE 5 Illustrating the dominant influence of the barytes filler on the modulus of polyurethane rubber and the variation of this property with equilibrium water content.

Figure 7 compares the effect of a 4.3% water content (case B) on the dynamic modulus of the filled material by comparison with a dry control specimen (case A). The transition at 0°C was confirmed as being due to the freezing of liquid water when it was found to remain unchanged at this temperature over two decades of frequency. No evidence of such a discontinuity was observed at

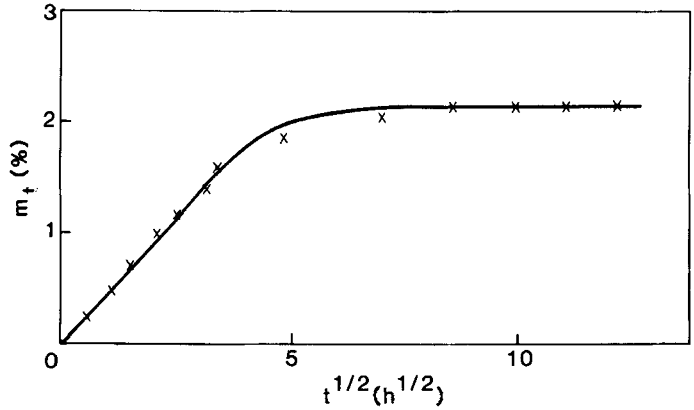

FIGURE 6 Water take-up for the unfilled polyurethane versus root time.

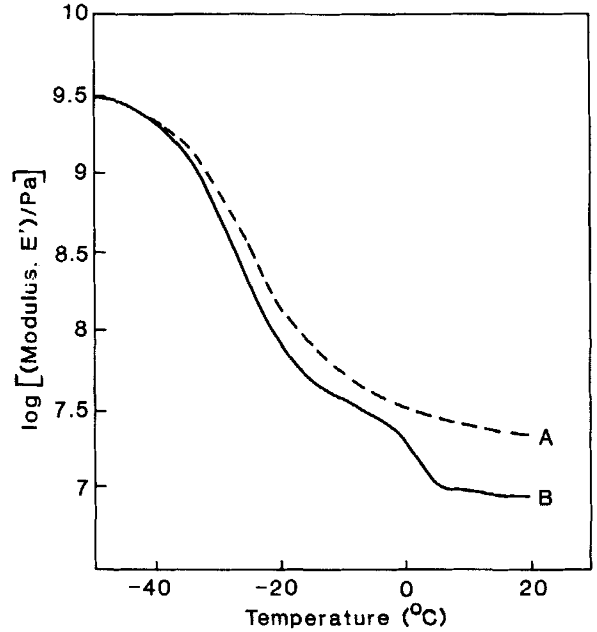

FIGURE 7 Log modulus versus temperature for filled polyurethane showing a transition at 0°C.

equilibrium water contents of <1.8% although this may merely reflect the relative insensitivity of the detection method.

The absorption of water to levels in excess of the solubility limit in the unfilled polymer was clearly attributable to the presence of the fillers and in particular with the barytes which was found to contain small quantities of water soluble material. Analysis showed these materials to be mainly chlorides, the most important being calcium chloride (~590 ppm), sodium chloride (~70 ppm) and magnesium chloride (~40 ppm). It was inferred that once the solution activity level for the soluble salts had been attained in the region of the fillers then osmotic processes commenced and these were responsible for the higher water absorption levels.

At water content levels of up to ~1.8% depression of peak damping temperature was proportional to water concentration and a plot of these results (Figure 8) closely follows the depression of

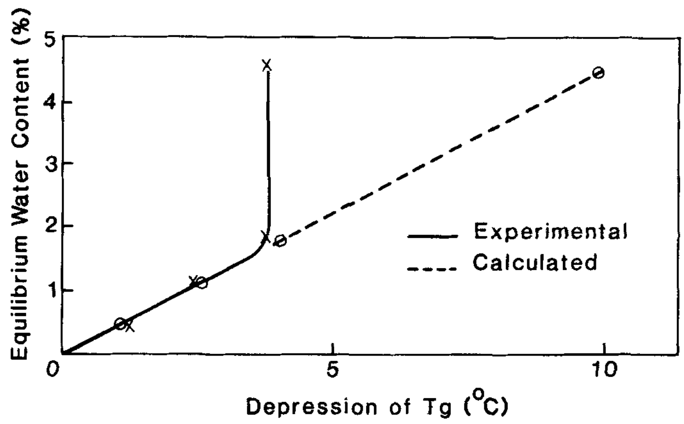

FIGURE 8 Depression of peak damping temperature by sorbed water and corresponding T_g depression calculated from the Fox Equation.

the T_g, as predicted by the Fox equation:[3]

$$\frac{1}{T_g}=\frac{W_A}{T_{g_A}}+\frac{W_B}{T_{g_B}}$$

where T_g is the glass transition temperature of the mixture and T_{g_A} and T_{g_B} are the respective T_g's of the two miscible components.

For the purposes of this calculation the peak damping temperature of the dry material at 10 Hz was taken to be the T_g. The T_g for water was assumed to be 135° K[4] and experimental values for peak damping temperature were obtained from DMTA. At higher water contents no further depression of peak damping temperature was observed, perhaps because of the commencement of clustering. On redrying from 4.3% water content, original properties were recovered, indicating that the effect of water was reversible.

It was thought possible that the dissolution of the water-soluble material associated with the barytes filler could have lead to the generation of gross mechanical discontinuities which could have been responsible for some of the observed property degradation, especially if these soluble salts were distributed over the surface of the reinforcing filler. A specially purified barium sulphate, believed to be relatively free of water-soluble material, was therefore investigated as an alternative. Because of its higher specific surface area this alternative filler was used at the lower level of 150 phr to fill a polyurethane rubber. This rubber was different from that used earlier only in that a purer form of the isocyanate was employed.

Both unfilled and filled specimens were allowed to equilibrate with water at laboratory temperatures after which modulus ($E'_{20\%}$) values were determined. Although the unfilled material was virtually unaffected, the modulus of the filled product was reduced by ~54%. By comparison, although the modulus of the earlier version of the unfilled rubber using the less pure isocyanate was also apparently unaffected after exposure to similar conditions, the material filled with soluble salt-containing barytes lost ~69% of its static modulus.

As an alternative to barium sulphate, ferric oxide was also considered as a filler for this polyurethane system. The use of such a filler was attractive partly because silane adhesion promoters could also be incorporated with the hope that the effects of attack by water could be reduced.

The investigation of the performance of iron oxide as the filler was preceded by an examination of the effects of the presence of the silane which was to be employed as the adhesion promoter in the urethane/iron oxide composite. The silane used was γ-aminopropyltriethoxysilane and five unfilled rubber formulations containing from 0 to 3.0 phr of the silane were prepared. In order to maintain stoichiometry, isocyanate content was increased to compensate for amine-terminated silane additions.

The modulus values for these materials, obtained after equilibration with water under conditions of 100% relative humidity, are compared with control values obtained from dry specimens in Figure 9. It can be seen that the modulus of the dry material falls with increasing silane content. This trend is probably the consequence of internal plasticisation of the rubber by bulky pendant silane groups. The rather lower modulus values found for the wet specimens reflect the additional plasticising effects of the ~1.83% equilibrium water content.

Iron oxide-filled versions (51.2% w/w) of each of these formulations were then prepared and modulus values for the dry controls are plotted against silane content in Figure 10. Here it can be seen that there is a significant increase in modulus with increasing silane content which is in sharp contrast with the results obtained with the

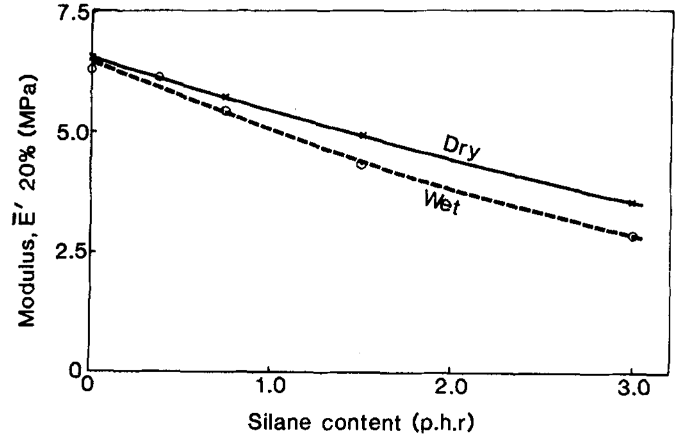

FIGURE 9 The static modulus versus silane content for an unfilled polyurethane comparing wet results with dry control values.

unfilled materials. The implication is that the progressively increasing potential for chemical coupling across the polmer matrix/filler interface is associated with progressively improving mechanical coupling and increasing modulus.

Specimens of iron oxide-filled material containing 0 phr and

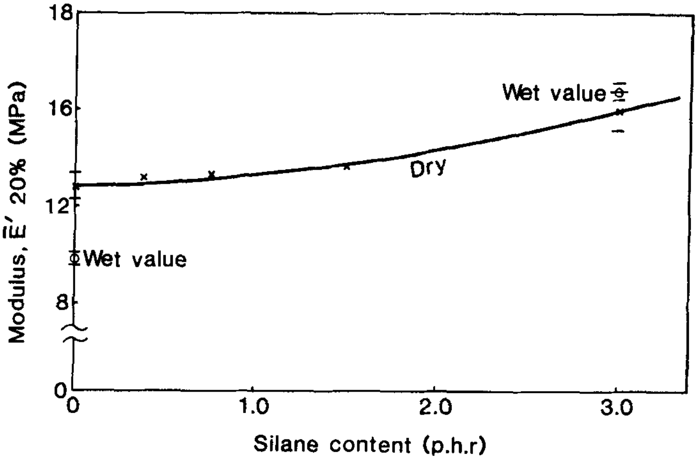

FIGURE 10 Static modulus versus silane content for an iron oxide-filled polyurethane.

3.0 phr of γ-aminopropyltriethoxysilane were immersed in water and, after a period of 240 days, it as noted that, although the composition without silane had suffered a modulus reduction of some 23%, the silane-containing specimens had remained unaffected. These results are also presented in Figure 10. Ninety-five percent confidence limits are also indicated for certain results.

Material was also prepared in which the iron oxide filler was pre-treated with the silane prior to incorporation in the urethane mix. This approach also leads to the production of specimens which were hydrolytically stable under similar conditions of test.

CONCLUSIONS

The presence of small equilibrium water content levels (~0.7%) causes the loss of most of the mechanical properties attributable to the presence of barytes filler in a polyurethane rubber, apparently as the result of the reversible disruption by water of polymer/filler adhesion. This water content is significantly less than the ~1.1% which results from seawater immersion.

This water concentration is approximately twenty-six times that required to provide a monomolecular layer over the entire filler surface and results show that the bulk of this water is associated with the polymer content rather than with the filler. Assuming that not more than two or three molecular layers would be required to cause loss of adhesion between adhesive and adherends it is concluded that, at lower equilibrium levels, water concentrates at hydrogen bondable sites perhaps within the polymer rather than at the polymer/filler interface.

At water activities equivalent to 98% relative humidity and less, water take up is limited in this way by the polymer content of the filled composite to a value of ~0.9% (equivalent to ~2.2% on the unfilled material which is close to the water solubility limit). When immersed in liquid water, however, water activity within the composite appears to be sufficiently high to lead to the solution of soluble species associated with the fillers and higher water contents are achieved as a consequence of the operation of osmotic processes. At these higher water content levels the additional water concentrates around the filler particles and behaves in a liquid-like manner.

Iron oxide-filled polyurethanes appear to be less sensitive than are barytes-filled systems to attack by water and when a silane coupling agent is used, either as an addition to the resin mix or as a pre-coat on the filler particles, an even greater hydrolytic stability is demonstrated.

Acknowledgements

The assistance of Mrs. H. J. Jordan and Mrs. T. S. Pratt in the production and evaluation of materials is gratefully acknowledged as is the contribution of Mr. J. R. Trayler who carried out the inorganic analyses. Surface area determinations were undertaken by Coulter Electronics Ltd.

References

1. J. Crank, *Mathematics of Diffusion—2nd edition* (Oxford University Press, UK, 1975).
2. A. L. McClellan, and H. F. Harnsberger, *J. Colloid Interface Sci.* **23,** 577 (1967).
3. T. G. Fox, *Bull. Amer. Phys. Soc.* **1,** 123 (1956).
4. M. Sugisaki, H. Suga and S. Seki, *J. Chem. Soc. Japan* **41,** 2591 (1968).