

out of the holes. In the second, they are assumed to be held at the other end and forced to break. In both cases the adhesive is treated as an elastic solid.

Theoretical relations have been derived from the work :

$$G'_a = G_a [1 + 4 \Phi(l/a)]$$

where Φ is the total area of holes per unit area of substrate surface, and l is the depth, and a is the radius of a hole.

When the pores in a substrate interconnect, then there is no way of pulling out a strand without breaking it. This situation arises when an adhesive permeates cloth, for example. An additional term is then required on the right-hand side of equation : $l\Phi U_b$, where U_b is the work required to stretch unit volume of the adhering material up to the point of rupture.

Experimental measurements with layers of rubber, about 1 mm thick, molded in contact with porous aluminum plates and stainless

steel wire woven cloth, are compared with these theoretical predictions. Two different elastomers were used : natural rubber and SBR, having values of breaking energy, density U_b of 19 and 3 MJ/m³, respectively.

In all cases, reasonable agreement was obtained between the measured values of the work G'_a required to pull off and overlying layer of the adhesive and values calculated on theoretical grounds, using equation. The apparent work of detachment was increased by up to 20 times for deep holes (of small radius). It should be noted that the apparent work of detachment can exceed the work of rupture of the adhesive layer itself, without any of the material actually breaking.

When the strands broke instead of pulling out, however, the extra work was as much as several hundred times the (low) work of detachment from a smooth surface. In this case, the additional work is proportional to the depths of the holes only, and thus it becomes the dominant term for deep pores.

A.D. Roberts

Developments in Understanding Rubber Adhesion*

This review of our Laboratory's work deals with three main areas of investigation : the adhesion of unbonded « uncured » rubber, bonding and the adhesion of unbonded vulcanized rubber.

Good adhesion or « tack » against the roughened surface of a rigid material depends on flow to maximize intimate contact. The importance of flow was made obvious in a comparison of peel strengths against roughened PMMA for raw and vulcanized rubbers. Recent results for the contact time dependence of the mutual adhesion of different elastomers suggest the production of intimate contact by flow is not the only factor but that there might be limited interdiffusion. Natural and nitrile rubber can be made to bond together if the natural is first softened by the incorporation of polybutene as compatible extender in order to promote flow. Here the principle requirement for good adhesion is flow, subsequent vulcanization reactions then bonding the adherents. This contrasts with plasticized rubber which produces intimate contact but adhesion is poor due to a weakened interface.

The pressure sensitive adhesive industry was founded upon the use of NR as a polymer for solution adhesives, though now the trend is to waterbased dispersions. Factors affecting the development of tack using NR latex have been examined.

Just to lower the plasticity is insufficient, tackifiers are also required. An alternative approach could be to reduce the molecular weight of the latex particles by suitable chemical modification, though not too much reduction because the continued presence of entanglements are necessary.

Rubber to metal bonding forms a crucial part of rubber technology. At moulding temperatures, raw rubber is a viscous fluid so better flow and penetration into an abraded metal surface occurs.

Compounding ingredients are soluble in the rubber at these temperatures and do not form an interface barrier to adhesion. Non-polar rubbers simply vulcanized in contact with most metals show little or no adhesion. An exception is brass which forms strong bonds that can exceed the cohesive strength of the vulcanized rubber. This is widely utilized in the bonding of steel cords in tyres, for which curing systems have been developed to give good adhesion.

Rubber engineering components possessing metal inserts nowadays use polymeric adhesives to aid bonding during vulcanization. There are a diversity of these but the mechanisms whereby adhesion is obtained are not well documented. The fracture mechanics of rubber-metal bonds has been developed by defining a characteristic tearing energy. Peel tests can be used to determine this energy.

The polarity of epoxidized natural rubber increases with the level of epoxidation, which means an increased compatibility with other materials as measured by ply bond adhesion values. Due to high adhesion with PVC, ENR-50 is being utilised as a cover compound bonded to PVC core conveyor belting. Silane coupling agents are generally employed in NR to maximize silica reinforcement during vulcanization. With ENR-25 and ENR-50 high degrees of reinforcement are obtained with silica in the absence of coupling agents.

Vulcanized rubber can be cold bonded to metal provided suitable cements are used and the rubber surface is adequately prepared (clean, bloom free). The rubber usually has to be made more polar by treatment with sulphuric acid or hypochlorite solution.

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The adhesion of unbonded vulcanized rubber to various substrates has been studied extensively over the last two decades, there being a number of interests such as modelling interfacial failure of bonded components, and predicting the surface « stickiness » of vulcanized rubber articles. The general energetics approach has been applied to various cases of adhesion (and to friction).

Recent investigations on an extracted, chemically saturated vulcanizate (no bloom and reasonably inert), show that the dwell effect exists and continues over a very long period (years). More surprisingly, memory effects have been demonstrated for the contact of nitrile and EP rubbers against glass. Some of the increased adhesion that occurs as a result of contact dwell is retained when the rubber test-strip is detached from the glass and re-adhered, even to a different area of the glass. Hence, the memory appears mainly to be associated with the rubber. It is conjectured that rearrangement of molecules in the surface layer into more favourable configurations with respect to the glass may be involved.

The threshold energy for peeling of unbonded vulcanizates is influenced by the dwell effect, as may be expected, but if peel rates are low the dwell time variation cannot be studied readily. A theoretical estimate for this energy can be made in a similar way

to cohesive failure, though there are certain differences such as chain configuration near an interface and lower interfacial bond strength. The observations are consistent with the existence of a threshold energy determined by the interfacial bond strength and the long-chain molecular structure of the elastomer. This implies an energy for detachment greater than would be expected simply from surface energies. The energy increases with peel rate, as expected on the basis of viscoelastic behaviour. Broadly, the work of adhesion at higher rates is governed by an interfacial energy scaled up by a bulk dissipative factor, as foreseen long ago.

Good adhesion is more likely to result if the real of contact between joined surfaces can be maximized. For raw rubber flow can achieve this ; for vulcanized rubber the degree of intimate contact will depend on rubber softness and surface smoothness. At the interface, interactions may be physical or chemical in nature. Attractive forces for unbonded contacts are likely to be the Van der Waal's type, together with specific polar-polar and perhaps electrostatic contributions. Hot rubber bonding in which chemical reactions occur leads to covalent bonds. It is difficult to rank the various contributions in practice. Further, contaminants (liquids, bloom, dust) at an interface can greatly reduce adhesion and give rise to irksome variability in product performance.

L'industrie française de la transformation du caoutchouc dans son contexte national et international*

G. Bresson

Principaux traits de la situation économique française :

- La croissance économique française et ses principales composantes,
- La situation de l'industrie française et plus particulièrement de l'industrie automobile,
- l'évolution récente de l'investissement industriel et des résultats des entreprises, situation du commerce extérieur.

Présentation de l'industrie française de la transformation du

caoutchouc replacée dans son contexte économique général :

- structure de la profession,
- consommation des matières premières,
- évolution de la production,
- évolution du chiffre d'affaires et du commerce extérieur.

Cette 3^e partie a été consacrée à la présentation de quelques réflexions sur certains aspects des perspectives à moyen et long terme de l'industrie française de la transformation du caoutchouc, en se situant par rapport au contexte international en général et à l'accélération de l'intégration européenne en particulier.