

Rheological Properties of Rubber-Carbon Black Compounds and Boundary Conditions on Solid Surfaces*

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The flow properties of rubber compounds are quite complex in comparison to the behavior of thermoplastics or gum rubber.

In recent years, the author and his co-workers have sought to make serious studies of both the rheological properties of rubber compounds and of the character of the boundary conditions on metal walls.

Rheological Properties

Measurements of shear viscosities have been carried out with rubber compounds with varying levels of carbon black and with differing black particle size. At volume loadings of 20 % carbon black and more, the compounds exhibit yield values, Y , i.e. stresses below which there is no flow. The magnitude of Y increases roughly inversely with ultimate particle size.

Similar yield values are exhibited by polymer compounds containing other small particulates such as talc, titanium dioxide, and calcium carbonate. Such polar particulates increase viscosities more and give higher yield values than carbon blacks of equivalent particle size.

Rubber compounds exhibit highly thixotropic behavior. The stress fields at the start of flow strongly depend upon time and previous history. The longer the rest history, the greater the stress overshoot in the transients.

Stress relaxation following a sudden strain or shear flow leads to a finite rather than a zero asymptotic stress.

Extrudate swell of rubber compounds is quite low and decreases with decreasing particle size and increasing particle loading. The compounds generally exhibit improved extrudate surface quality. The magnitude of swell from slit dies is greater than that from capillary dies.

Boundary Conditions

It is found in experiments using pressurized rotational rheometer similar to that of Turner and Moore (8), that when the applied pressure on an elastomer or rubber compound is reduced to 0.2 MPa, a lower slip is initiated. The slip is observed both in the reduced magnitudes of torque and in the markings on rubber caps removed from rotors. Slip is initiated at outer radii and propagates radially inward.

The levels of stresses extended by rubber compounds on rotors made from different materials vary depending upon the nature of the surface and its roughness. This is most clearly seen at low levels of imposed pressures. For smooth rotors, it was found that stresses order as :

Copper
Brass > aluminum > Steels > PTFE

At higher pressures, smooth and grooved rotors from different materials (except for PTFE, which is usually lower) give similar values. However, a system, filled with 7 percent stearic acid gave lower stresses on smooth as opposed to grooved rotors. This indicates the existence of a thin layer of lubricant on the surface of the rotor.

Slippage was also induced in the extrusion of rubber compounds by using porous metal dies and injection pressurized air. Experiments were carried out using various die systems attached to a cold feed rubber extruder.

The air pressure required to create a lubricate air layer and cause substantial drops in extrusion pressure was of the order 0.25 MPa.

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Effect of Surface Roughness and Mechanical Interlocking on Adhesion*

The apparent strength of adhesion has been measured for a soft elastic layer of rubber, adhering to model porous substrates, consisting of rigid plates containing regular arrays of cylindrical

holes. Two contributions to the apparent strength have been identified and compared with the predictions of a simple theoretical treatment. In one case the strands of adhesive are assumed to pull

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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.

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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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