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Effect of bulk deformation on rubber adhesion

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Abstract

In general, rubber friction is divided into two parts; the bulk hysteresis and the contact adhesive term. These two contributions are regarded to be independent of each other, but this is only a simplified assumption. If the adhesive force is solely a function of the surface free energy, it has been assumed that this adhesive force per unit area should be constant during any bulk (surface) deformation. The surface free energy is a function of both internal energy and entropy, and so it should change if the internal energy and/or entropy are changing due to any bulk deformation. In order to ascertain the effect of the bulk deformation on rubber adhesion, this effect on the surface free energy of two rubber compounds filled with various loading fractions of carbon black, natural rubber (NR) and styrene butadiene rubber (SBR) was studied. The surface free energy was determined from measured contact angles on rubber samples at constant applied strain. It was found that the surface free energy increases significantly upon applying a deformation. However, with increasing the carbon black loading fraction the surface tension increase becomes less pronounced. The effect of the surface free energy on the surface damage generated by scratch tests was also discussed. It was found that roll debris formation occurs only in the case of the rubber compounds whose apparent surface free energy increases greatly after applying large bulk deformations.

Keywords: Roll formation; Surface energy; Wear mechanism

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1. Introduction

Improvement in the durability of rubber compounds is one of the most important research areas in order to improve the quality of tyres. The durability of the tyre tread is generally thought to be affected by the wear resistance of the tread rubber compound. Since rubber wear coincides with rubber friction, it is very important to ascertain the corresponding mechanism of rubber friction. In general, rubber friction is divided into two parts; the bulk hysteresis and the contact adhesive term [1]. It is accepted that the rubber friction is a function of the viscoelastic properties of the bulk rubber [2,3]. Hysteresis friction is considered to be caused by the bulk deformation that occurs during friction, i.e. the deformational loses [4], which is a function of the bulk viscoelastic properties of the rubber. The origin of adhesive friction, however, is much more complicated not least because of the surface roughness of the counterparts and rubber materials.

Grosch found that the maximum of the adhesive component of rubber friction on a smooth surface occurs at a sliding velocity, which correlates to the reduced frequency corresponding to the maximum of the loss modulus [2]. Ludema and Tabor considered the adhesion of rubber compounds to be a combination of the true contact area and the shear strength within the thin surface layer [3]. Schallamach explained the dependency of rubber friction on the viscoelastic properties by applying a thermally activated rate process model [5]. His calculation indicates that the adhesion component of rubber friction is a function of the true contact area as he demonstrated by model experiments [6]. Schallamach observed that a tangential force, which is applied to a hemispherical rubber sample on a clean smooth surface, causes the contact surface of the rubber to buckle and generate waves of detachment [7]. It was suggested that energy must be supplied to the system to keep the waves moving along the surface to overcome the peeling energy losses.

Briggs and Briscoe showed that the work of adhesion in a peeling process is the main energy loss [8] and is a function of peeling velocity and surface roughness [9]. The dependency of the work of adhesion on the peeling velocity suggests that the adhesion component of rubber friction may be a function of the viscoelastic properties. Ideally the adhesion of rubber compounds can be considered as a function of surface free energy, if the surface damage and bulk damage could be avoided [10].

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In this case, the rubber adhesion is thought to be a reversible process [11]. Thus, the rubber adhesion is considered to be a function of the viscoelastic bulk materials properties and the surface free energy.

These two processes of rubber friction are often thought to be independent of each other, but this is only a simplified assumption. The viscoelastic dissipation should be caused by bulk/interface deformation, and so it seems to suggest that both adhesion and deformation occur at the same time as response to the same external stimulus. The peeling or shear stress seems to be independent of the bulk deformation, which affects the hysteresis loss because of the different volume of the corresponding region during the deformation. However, in this case it is based on the assumption that the strength of the junction between the rubber surface and the counterpart is constant during the deformation. Gent and Petrich suggested that a better correlation between the experimental peel strength and the theoretical strength calculated from the experimental stress–strain curve can be obtained if the value of the strength of the interaction between the rubber surface and the counterface could be varied with the deformation rate instead assuming it to be constant during the bulk deformation [12].

The surface free energy γ_s at constant pressure and volume is described as;

$$\gamma_s = \left(\frac{\partial G}{\partial s}\right)_T = \left(\frac{\partial A}{\partial s}\right)_{T,V} = \left(\frac{\partial U}{\partial s}\right)_{T,V} - T\left(\frac{\partial S}{\partial s}\right)_{T,V} \quad (1)$$

where G is the Gibbs free energy, A the Helmholtz free energy, U the internal energy, T the absolute temperature, S the entropy, V the volume and s the surface area. Eq. (1) shows the surface free energy is a function of both internal energy and entropy.

The elastic force of rubber compounds is also considered to be a function of both internal energy and entropy. If a rubber compound is uniaxially deformed at the same temperature, the responding force F is;

$$F = \left(\frac{\partial A}{\partial l}\right)_T = \left(\frac{\partial U}{\partial l}\right)_T - T\left(\frac{\partial S}{\partial l}\right)_T \quad (2)$$

where l is the stretched length. Eq. (2) links both the internal energy U and entropy S with the material deformation produced by an applied stress. This implies that the surface free energy γ_s of a substrate should be a function of the imposed strain. Clarifying the effect of bulk deformation on the surface free energy of rubber materials might help to explain the rubber friction.

We discuss the effect of bulk deformation on the surface free energy of rubber compounds and its relation to the surface damage mode. We are also aiming to relate the change in the surface free energy of rubber compounds to the roll debris formation (as defined in [13]) during scratching friction.

2. Experimental

2.1. Materials

All rubber compounds used in this research were kindly supplied by Bridgestone Corporation (Japan). Table 1 summarises the composition of the various rubber samples. The rubber sheets of thickness 2.0 mm were cut into 2.0 cm × 7.0 cm rectangular specimens. Prior to any measurements the surfaces of the rubber samples were carefully cleaned using diethyl ether (99.9%, Aldrich) and then dried [14]. In the cases of the prestretched samples, they were cleaned by wiping using diethyl ether soaked fluff-free tissue paper after stretching in order to remove additives, which might have migrated from the bulk to the surface.

Table 1
Composition of materials (parts by weight)

	Series of NR	Series of SBR
Natural rubber	100.06	
Styrene-butadiene (24/76)		100
Carbon N234	0, 15, 30, 45, 60	
Aromatic oil	10	37.5
Stearic acid	3	1
Zinc oxide	5	3
Sulfer	2.5	1.5
N-tert-Butyl-2-benzothiazolyl sulfenamide	0.5	
Dibenzothiazyldisulfide		1.5

2.2. Contact angle measurements

Low-rate dynamic contact angle measurements on sessile drops were measured using Drop Shape Analyser (DSA 10 MK2, Krüss GmbH, Hamburg, Germany). Only the advancing contact angles were determined. The advancing mode, i.e. wetting of dry surface, was realized by putting sessile water droplets of about 7 μL on the rubber surfaces and increasing the volume of liquid in the drop by using a motor driven microsyringe. The rate of droplet expansion was 10 μL/min. At least 10, but more often 20, independent measurements at different sites of several samples were taken. The largest and smallest contact angle values in each series were discarded and standard deviations obtained. The contact angles were measured using deionised water, formamide (99.5+%, Aldrich) and diiodomethane (99%, Aldrich). All measurements were conducted in an air-conditioned room at 20 °C.

Contact angle measurements were also performed on uniaxially prestretched rubber compounds in constant strain mode. The specimens were stretched by 100, 300 and 700% strain, respectively. The samples were stretched by a bench vice. Once the desired strain was adjusted the vice was fixed. The major difficulty is the polymer relaxation occurring in the elongated rubber specimens. However, in a rubber compound the polymer main chains are “locked in place” by covalent crosslinks formed during the vulcanisation process, which leads to rather long relaxation times so we assumed that the applied strain is constant.

2.3. Determination of the surface free energy

Solid surface free energies are commonly estimated using surface tension models from measured contact angles of series