ON THE FRACTURE MECHANISM IN FILLED RUBBERS

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Possible fracture mechanisms in filled rubbers are examined in the light of the adhesion theory of elastomer reinforcement. The cases of rubbers containing inactive fillers, when the crack grows along the elastomer-filler boundary, and rubbers containing active fillers, when the crack propagates through the polymer, are considered. The effect of the presence of chains of filler particles on the fracture mechanism is examined.

In our publications on the development of an adhesion theory of elastomer reinforcement [1] we have described the effect on the reinforcement of filled elastomers and the adhesion of elastomers to fillers of such factors as the duration and temperature of polymer-rubber contact [2], the degree of vulcanization of the elastomer [3], the molecular weight of the elastomer [4], the polarity of the elastomer [5], the chemical modification of the filler surfaces [1], and the introduction into the rubber mix of special adhesive and adhesive additives [4].

However, no examination of the role of adhesion effects in elastomer reinforcement would be complete without a discussion in the light of these new ideas of the fracture mechanism of filled rubbers.

The literature on the fracture mechanism of unfilled rubbers is quite extensive, and several excellent reviews are available [6]. However, much less attention has been paid to filled rubbers [7-18] despite their great practical importance.

However, before proceeding to examine the fracture mechanism of filled rubbers from the standpoint of the adhesion theory, we will first consider the necessary premisses of such an inquiry.

1. Starting from the generally accepted view of multicontact adsorption of polymer molecules at the surface of active filler particles, it is clear that given a relatively small distance between filler particles (in ordinary rubber mixes it is approximately 200 Å [19]), a single linear macromolecule may bind two or more neighboring particles. It may be assumed that in this case the binding mechanism is very similar to that which according to modern ideas is responsible for the flocculation of colloidal particles when high polymers are introduced into lyosols [20, 21]. There is also direct evidence that flocculation (the formation of a carbon-rubber gel) takes place when carbon black is introduced into a rubber. Probably the only difference between flocculation in filled rubber mixes and flocculation in lyosols consists in the fact that, since the distances between filler particles are small and the length of the macromolecule may reach thousands of angstroms, a single molecular chain may cross from the surface of one particle to the surface of another not once, but many times. It is important to note that in the layer of polymer between filler particles the molecular chains must be to a certain extent oriented parallel to the axis through the centers of the particles, and thus the elastomer molecules in such a gap will be in a more or less ordered state.

2. Only fillers whose particles independently possess high mechanical strength, at any rate greater than that of the polymer, are capable of acting as reinforcement. In other words, a filler is capable of reinforcing a polymer only if the failure of the rubber is not accompanied by failure of the filler particles themselves. Of course, it does not follow that any filler whose particles possess good physico-mechanical...
properties is capable of reinforcing rubbers. Naturally, for a filler to exert a reinforcing effect high polymer-filler adhesion is also necessary.

3. The failure of deformed rubbers always occurs as a result of overstressing at microdefects with subsequent crack propagation. This view, first formulated in relation to the failure of brittle materials [22], has since been widely applied to polymer systems [23].

4. Our last postulate concerns the causes of the strengthening of systems containing active fillers. The propositions formulated above make it possible to give a perfectly definite answer to this question. In fact, if we start by assuming that the failure of the system is purely cohesive in nature, the polymer in the gap between neighboring filler particles must offer increased resistance to a growing crack, since the macromolecules in the gap are preferentially oriented at right angles to the direction of crack propagation. At the same time, the crack cannot grow in a direction parallel to the orientation of the macromolecules, since this is prevented by the stronger filler particles that bound the gap. This theory is in good agreement with modern ideas on the effect of orientation of the molecular chains on the strength of polymers. If it is assumed that the failure of the system is adhesive in nature, then, obviously, the reinforcing effect will be the greater, the greater the adhesion to the filler, i.e., the more active the filler. The situation remains the same if we assume a mixed type of fracture, when zones of cohesive failure alternate with zones of adhesive failure.

We now proceed to a direct examination of the fracture mechanism of filled rubbers.

When a polymer specimen consisting of long flexible molecules fails, either the chain molecules break or the intermolecular forces are overcome, and in the latter case the molecules will be displaced relative to each other or pulled apart. Naturally, the fracture mechanism will depend on which type of bond is weakest in the particular circumstances of a given test.

In the case of filled rubbers there is one more possibility of failure — failure along the filler-polymer boundary, i.e., adhesion failure. Since the polymer is the external phase of the system, zones with this type of failure must alternate with zones of purely cohesion failure of the polymer. The question arises how likely is the adhesion failure of filled rubbers. We will consider this question separately for rubbers containing fillers with different degrees of activity.

Fracture Mechanism of Rubbers Containing Inactive Fillers. Naturally, when the polymer-filler interaction energy is very small, i.e., when the adhesion of the polymer to the filler is close to zero \((\text{Ad} \approx 0)\), a crack formed in the rubber at the site of a microdefect, upon encountering a filler particle, will easily penetrate along the phase interface. In the case of a rubber with an inactive filler this fracture mechanism is determined by the fact that the greatest stresses always occur at the polymer-foreign body boundary. The stress concentration around filler particles in a deformed rubber has been experimentally investigated by Green [9], Kruse [10], Andrews and Walsh [15], and Prestridge [16]. Observations with a polarizing microscope have shown that zones of high stress are formed around the filler particles. In the case of sufficiently large particles of an inactive filler (several microns in size) it was possible to observe the separation of the polymer from the surface of the particles and the formation of vacuoles. Vacuole formation around inactive filler particles was especially clearly demonstrated in [24].

Thus, the presence of an inactive filler should lead to a reduction in strength. The increased stiffness of rubbers containing inactive or only slightly active fillers is attributable to the partial filling of the system with hard particles. In this case the causes of the increased stiffness are similar to those responsible for the increased viscosity of a liquid into which hard nondeformable particles are introduced.

Fracture Mechanism of Rubbers Containing Active Fillers. If the interaction between the filler and the polymer is sufficiently strong, but the adhesion is less than the cohesion strength of the polymer in the layers between filler particles \((0 < \text{Ad} < \text{Coh})\), then the general picture of rubber failure under deformation will be outwardly similar to that observed in a system containing inactive fillers. In [9-16] it was shown that upon encountering active filler particles a crack usually propagates along the interphase boundary. According to Prestridge [16], a crack in rubber crosses, as it were, from one particle to another; upon encountering a particle, the crack bypasses it, so that in an electron photomicrograph one can either clearly distinguish the surface of the particle itself or see a depression in the polymer corresponding to the particle.

In the case of the deformation of rubbers containing active fillers failure along the rubber-filler boundary is attributable, firstly, to the stress concentration at that boundary [16] and, secondly, to the fact...