

# The mechanical properties of rubber compounds containing soft fillers

## Part 2 *Tear properties*

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A detailed examination of failure of properties of polybutadiene containing soft elastomeric fillers has previously been described [1]. Here the effect of filler modulus and filler-matrix adhesion on tear strength is measured. Tear behaviour depends upon the level of interfacial adhesion; when high, tear strength increases with increasing filler hardness, but if interfacial adhesion is low, incorporation of fillers may result in low tear strengths. An estimate of the edge flaw size is made from the tear strength and strain energy densities at break. It was found that compounds with low interfacial adhesion generally had edge flaw sizes of the same order as the maximum filler particle size. A correlation between tear strength and tear surface morphology is made.

### 1. Introduction

The mechanical properties of rubber compounds containing reground rubber filler have been described in a previous paper [1], with particular attention being paid to the effect of filler modulus and filler to matrix adhesion. It was found that significant reduction in mechanical performance arose when the interfacial adhesion was low and/or the filler was excessively hard. In this paper we describe the influence of these parameters on the tear strength of these materials. A brief review of similar work with glass-bead filled elastomers is given below.

#### 1.1. Tear strength of elastomers containing glass beads

Incorporation of glass beads into polybutadiene (BR) results in improved tear strengths. This reinforcement is greater for smaller particles [2] but appears to be independent of the degree of bead to matrix bonding (for beads of 150  $\mu\text{m}$  diameter) [3].

Large beads reinforce the elastomer by causing tear deviation [2, 3]. Small beads, however, cause little deviation, reinforcement instead being attributed to the increased contribution of the surface energy to tear energy [2].

Using an extension of Griffiths energy balance (Equation 1),

$$U'_b = T/2kc \quad (1)$$

Dreyfuss and co-workers [2, 3] calculated the size of the edge flaw initiating failure. In Equation 1,  $T$  is the tear energy,  $U'_b$  is the strain energy density at break,  $c$  is the edge flaw and  $k$  is a constant. For moderate bead diameter ( $> 100 \mu\text{m}$ )  $c$  approaches the size of the largest beads present. If the beads are large (1000  $\mu\text{m}$ )  $c$  corresponds to the inter-bead spacing. Flaw size was also shown to decrease as bead to matrix bonding increased.

#### 1.2. Tear strength of elastomers containing recycled rubber crumb

Although the tensile properties of these materials has been widely reported, tear behaviour has received little attention. Burgoyne and Leaker [4] have shown that incorporation of crumb, with the same composition, causes little change in the tear strength of the "parent" compound at loadings of 10% or less. In similar studies, Peterson *et al.* [5] found that tear strength fell considerably at higher loadings (20 to 40%). Tear strength was also observed to increase slightly with decreasing crumb particle size.

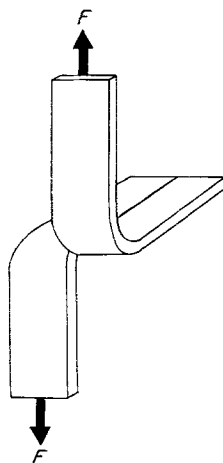


Figure 1 Tear test specimen.

## 2. Experimental details

The preparation of filler and host compounds has been described elsewhere [1]. Four fillers (A to D) ranging in hardness from 31 to 72 Shore A degrees were incorporated into two BR masterbatches, at loadings of 2.5 to 25 vol%. The Type 1 masterbatch was an unfilled BR while Type 2 contained 50 wt % carbon black.

### 2.1. Tear strength and hysteresis determination

Tear strengths were determined using trouser tear specimens similar to that shown in Fig. 1. Each was approximately 2 mm thick and 20 mm wide, and scored to half thickness along a centre line so that the tear width was approximately 1 mm. Tear energies,  $T$ , were calculated using Equation 2 with the measured tear force being  $F$  and tear width,  $w$ . A grip separation rate of  $5 \text{ mm min}^{-1}$  was used.

$$T = 2F/w \quad (2)$$

In order to determine  $U'_b$  (Equation 1), the strain energy density at break  $U_b$  and the hysteresis,  $H$ , must be known.  $U_b$  has been previously determined [1]. Hysteresis was determined by straining each tensile dumb-bell to an elongation just short of breaking, then unloading it at the same rate.  $H$  was then calculated from Equation 3:

$$H = (A_1 - A_2)/A_1 \quad (3)$$

where  $A_1$  is the area under the loading stress-strain curve, and  $A_2$  is that under the unloading curve.  $U'_b$  is then calculated using Equation 4:

$$U'_b = U_b(1 - H) \quad (4)$$

## 2.2. Microscopy

Specimens for optical microscopy were prepared by dispersing a small amount (0.2 g) of fillers A or D in 60 g Type 1 masterbatch in an internal mixer. Compounds were then cured into 2 mm thick pads from which small dumb-bells were cut. These were then tested on a small hand-operated straining device mounted under a "Nikon" stereo microscope.

## 2.3 Particle size analysis

Particle size distribution of the fillers was determined on a Zeiss Microvideomat II image analyser. Compounds were prepared in a similar manner to that in Section 2.2. They were then pressed between two stainless steel plates and cured. The resultant transparent pads contained a monolayer of black crumb particles and so were suitable for image analysis.

## 3. Results and discussion

### 3.1. Tear energy

The tear strengths of the filler and filled compounds are given in Table I. Although the results were averaged over the tear length, variations of 10 to 20% were not uncommon. Incorporation of the hardest fillers into the Type 1 masterbatch resulted in improved tear strengths. Electron micrographs of the tear surfaces (Fig. 2) showed that they were somewhat rougher than that of the unfilled masterbatch. The presence of the softer fillers C and D caused little change in the tear properties of the compound. Both the tear strength (Table I) and the tear topography (Fig. 2d) were similar to those of the unfilled com-

TABLE I Tear strengths

Filler	Masterbatch	Code	$T$ (kJ m <sup>-2</sup> )
A	—	A	3837 ± 241
B	—	B	2317
C	—	C	2132 ± 423
D	—	D	1763 ± 317
—	1	1	1145
A	1	1A/25	1779 ± 334
B	1	1B/25	1919 ± 305
C	1	1C/25	1230 ± 7
D	1	1D/25	
—	2	2	4117 ± 483
A	2	2A/25	2798 ± 437
B	2	2B/25	4033 ± 660
C	2	2C/25	4543 ± 322
D	2	2D/25	2944 ± 159

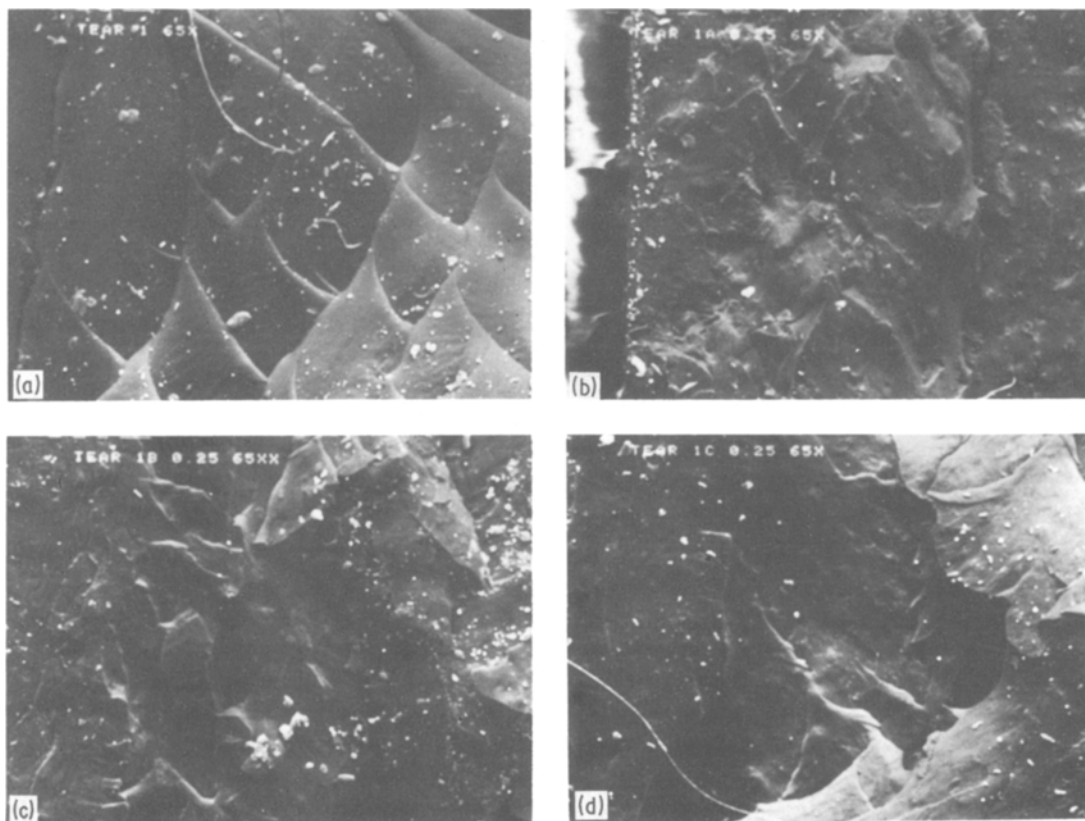


Figure 2 Tear surfaces of Type 1 compounds. (a) Masterbatch  $\times 39$ . (b) 1A/25  $\times 39$ . (c) 1B/25  $\times 39$ . (d) 1C/25  $\times 39$ .

pound. It appears that the reinforcement of the Type 1 compounds results from the increase in tear deviation, although some contribution from hysteresis effects within the filler is expected.

Type 2 compounds (which show poor filler to matrix adhesion) exhibit anomalous behaviour. Incorporation of the hardest and softest fillers (A and D) results in a lower tear strength. Given the rough appearance of the tear surface of compound 2A/25 (Fig. 3b) it is suggested that this is the result of low adhesion between the filler and the matrix material. In contrast to this behaviour, compound 2D/25 has a flat tear topography, indicating that it is the low filler tear strength which leads to the reduction in tear strength of the compound.

The relatively high tear strength of compounds 2B/25 and 2C/25 may be explained in part by their flat tear topography (Figs. 3c and d). This indicates that the filler contributes to the tear strength of these materials (rather than the filler–matrix interface) and because it is higher so is the tear strength of the compound. It was also observed that the tear deviated from the guiding

cut and proceeded through the thick section of the specimen, resulting in an increased contribution to tear strength by the strain energy term.

For Type 2 compounds containing filler A, it can be seen that tear strength increases as the loading decreases (Fig. 4). The solid line represents the values of tear strength calculated using Equation 5 [6]:

$$T = T_m(1 - \phi_f) + T_f(nK\phi_f) \quad (5)$$

where  $T$  is the tear strength and  $\phi_f$  is the filler volume fraction. Subscripts m and f refer to the matrix and filler. The constants  $n$  and  $K$  allow for the increased surface area of the filler on the tear surface. In this case  $T_f$  was made equivalent to the interfacial adhesive energy as determined in Part 1 [1]. Good agreement between experiment and theory is obtained when values of 1 and 1.5 are assigned to the constants  $n$  and  $K$ .  $K$  allows for the increased “surface volume fraction” of the filler: given the rough appearance of the surface a value of 1.5 does not seem unreasonable. This agreement further emphasizes the role of the interface in the tearing process.

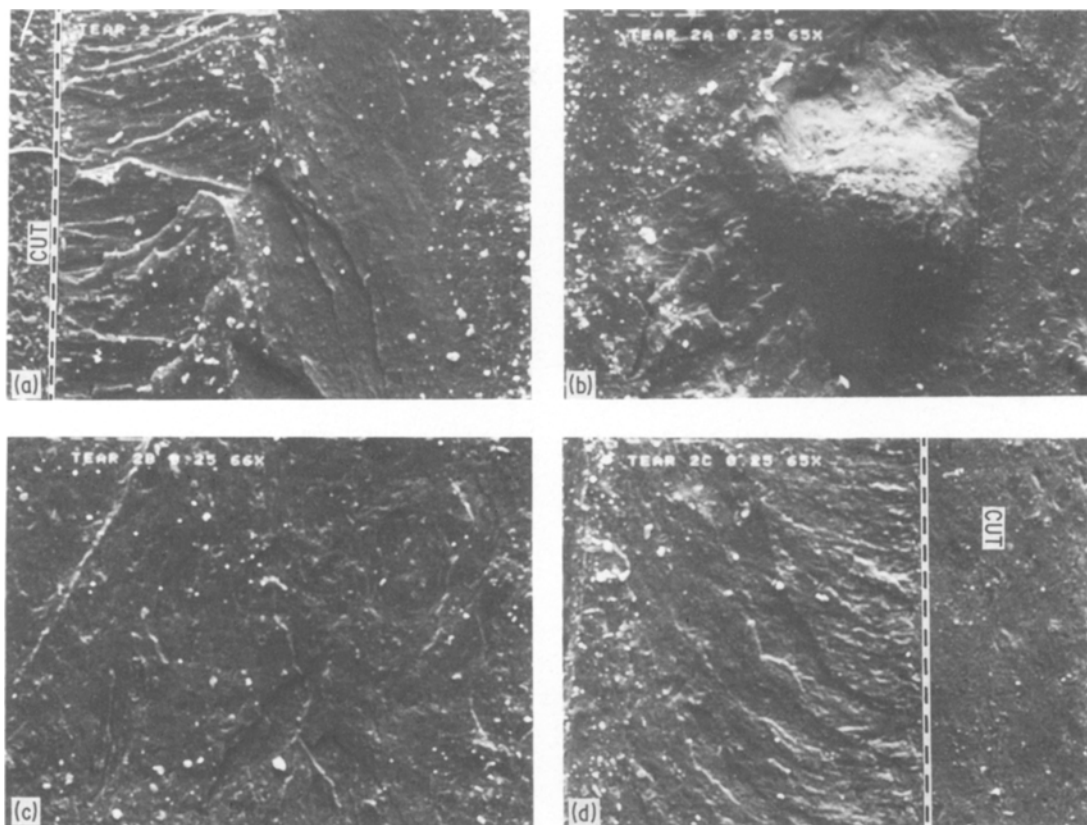


Figure 3 Tear surfaces of Type 2 compounds. (a) Masterbatch  $\times 39$ . (b) 2A/25  $\times 39$ . (c) 2B/25  $\times 39$ . (d) 2C/25  $\times 39$ .

A similar plot of tear strength for Type 2 compounds containing the softest filler D shows the same trend although the correlation with predicted values was less (Fig. 5). Because the tear surface was flat,  $T_f$  was made equivalent to the filler tear energy and a value of 1 was assigned to the constants  $n$  and  $K$ .

### 3.2. Fracture nuclei

Edge flaw sizes calculated using Equation 1 are given in Table II. Type 1 compounds were found

to have a hysteresis of approximately 30%, while Type 2 compounds had much higher values of about 70%, this being due to the presence of carbon black. Values of 2 and 1.5 were given to the constant  $k$  for the Types 1 and 2 compounds, respectively [7].

Table II shows two values for edge flaw size. The first,  $c$ , was calculated using the tear energy of the masterbatch and probably applies to those compounds showing little filler rupture (i.e. those containing the hardest fillers). The second value,

TABLE II Calculated flaw size

Code	$U_b$ ( $\text{kJ m}^{-3}$ )	$U'_b$ ( $\text{kJ m}^{-3}$ )	$T$ ( $\text{kJ m}^{-2}$ )	$c$ ( $\mu\text{m}$ )	$c'$ ( $\mu\text{m}$ )
1	3690	2583	1145	148	148
1A/25	2000	1400	1779	273	424
1B/25	3400	2380	1919	160	269
1C/25	4840	3388	1233	113	121
1D/25	3240	2268	1500	168	220
2	8770	2631	4117	522	522
2A/25	3580	1074	2798	1278	868
2B/25	4650	1395	4033	984	1064
2C/25	4780	1434	4543	957	1056
2D/25	7890	2367	2944	580	415

Figure 4 Tear strength of Type 2 compounds as a function of filler A loading.

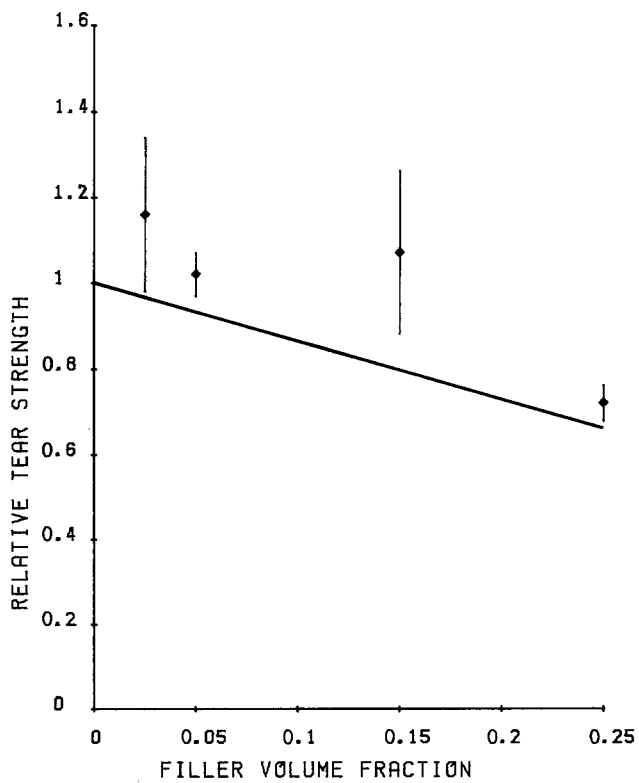
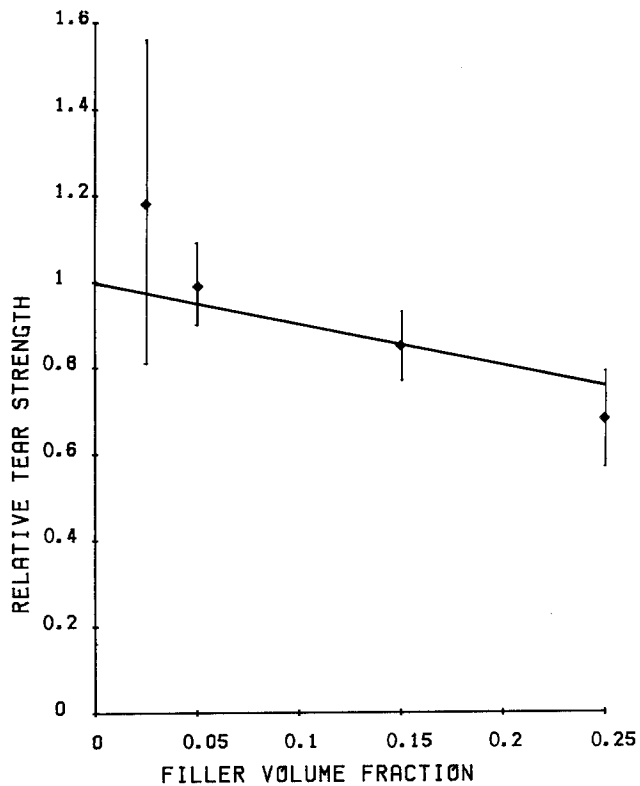


Figure 5 Tear strength of Type 2 compounds as a function of filler D loading.

TABLE III Particle size distributions

Diameter ( $\mu\text{m}$ )	Filler, cumulative weight percent			
	A	B	C	D
100	10	18	8	11
200	28	39	26	26
300	40	61	42	42
400	51	69	50	55
500	60	80	57	71
600	64	88	59	76
708	68	100	62	79
800	81	100	62	79
900	81	100	76	81
1000	81	100	85	81
> 1134	19	0	15	19
Average	336	296	465	309

$c$  (calculated using the actual compound tear energy), applies to the compounds containing the softer fillers, where filler rupture is predominant. Although the values differ slightly the trends are the same.

In Type 1 compounds the flaw size was of the same order as the inherent flaw size with the exception of that containing the hardest filler, A. The flaw size of this compound, which also had the lowest tensile strength, was found to be significantly larger.

All filled Type 2 compounds, except that containing the softest filler, D, were found to have a flaw size of approximately  $1000\mu\text{m}$ . This corresponds closely to the maximum filler particle size (see Table III). In compound 2D/25, which has the highest tensile strength, the flaw size was calculated to be the same as that of the unfilled masterbatch.

These results support the hypothesis that poor tensile performance results from dewetting of the filler by the matrix. In Type 1 compounds where

filler–matrix adhesion is high, only the hardest filler acts as a fracture precursor. The compounds also have high relative tensile properties. However, in Type 2 compounds all fillers, except the softest, act as fracture nuclei, leading to lower relative tensile properties. This may be attributed to the lower degree of filler–matrix adhesion. These materials fail when the voids, formed by interfacial breakdown, tear.

### 3.3. Microscopic studies

Optical micrographs of Type 1 compounds containing filler A (Fig. 6) show obvious dewetting. The denuded filler particle is clearly seen in the fracture surface and the radiating lines indicate that it was the fracture precursor.

Aggregate breakdown was also observed (as shown in Fig. 7). This process tended to take place at lower strains and also resulted in void formation which in turn led to failure of the materials. This is evident from the appearance of the resulting fracture surfaces (Fig. 7b).

When similar specimens containing the softest filler, D, were studied no microscopic evidence of filler dewetting before failure was found. This is in agreement with the previous calculations, which showed that the flaw size of these compounds is the same as that of the unfilled material.

## 4. Conclusions

It can be concluded from this work that the tear strength of the filled materials is dependent upon the filler hardness and the filler–matrix bonding. Given high filler–matrix adhesion the tear strength of the filled materials increases with filler hardness, this being attributed to a tear deviation mechanism similar to that found in the glass-bead filled elastomers. If interfacial adhesion is low, tear

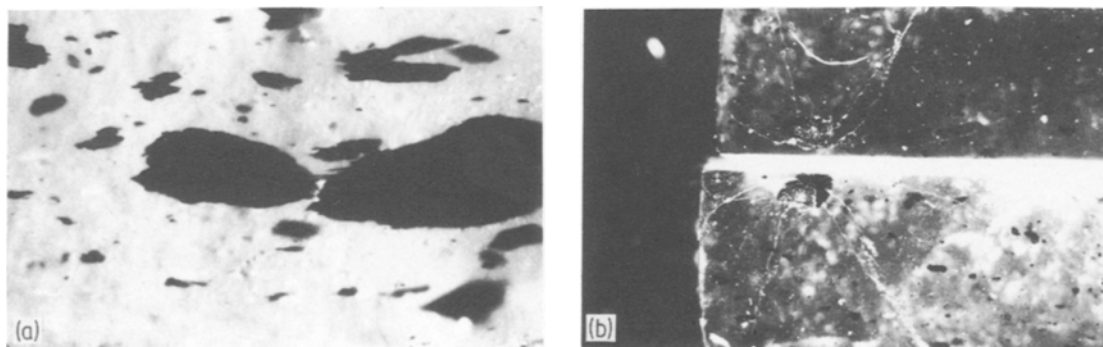


Figure 6 (a) Dewetting of filler particle whilst strained. (b) Corresponding fracture surface.

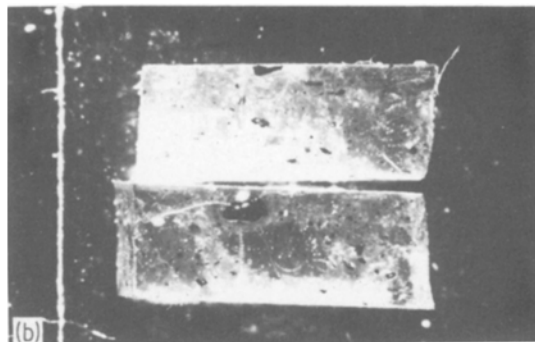
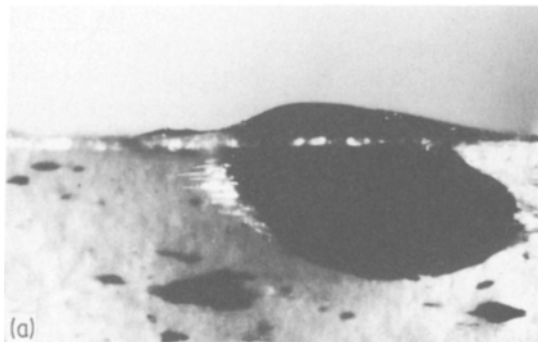


Figure 7 (a) Aggregate breakdown upon straining. (b) Corresponding fracture surface.

strength is found to fall, due to the increased importance of the filler–matrix interface in the tearing process. As filler hardness decreases, filler tearing becomes the predominant factor influencing the tear behaviour of these materials.

Theoretical calculations and microscopic evidence support the hypothesis that poor mechanical properties of the compounds are the result of filler dewetting. This causes void formation which leads to premature failure. Dewetting is predominant in materials which show low adhesion to the filler. It is also shown that dewetting is more likely to occur when the filler is hard.

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