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The mechanical properties of rubber compounds containing soft fillers

Part 1 *Tensile properties and fracture morphology*

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Rubber compounds are traditionally reinforced with carbon black or silica fillers of minute particle size. Prior studies in which much larger recycled rubber scrap has been incorporated, indicate that only low levels can be tolerated before significant deterioration in performance is noted. Failure can be superficially linked to macroscopic flaws as is commonly observed in both thermoplastics and elastomers. In this study a detailed examination of soft elastomeric fillers in a polybutadiene matrix is described. In particular the effect of filler hardness and interfacial bonding is stressed. An estimation of the interfacial adhesion is made from peel tests.

1. Introduction

1.1. Scope and aims

Previous studies on the use of recycled scrap rubber as a filler of rubber compound suggest that the observed deterioration in mechanical properties is caused by the poor adhesion between filler and matrix [1]. This paper presents an intensive study of the parameters influencing the performance of these materials. Ultimately it is hoped that this will lead to improved performance, so potentially increasing the use of scrap rubber as a filler.

The effect of particle size, modulus, and interfacial adhesion on the mechanical properties of elastomers containing hard fillers has already been studied, as has the effect of interfacial adhesion on the failure of two-phase elastomer blends. This work is briefly reviewed below.

1.2. Studies of hard fillers

In glass bead-filled polybutadiene (BR) systems ultimate tensile strength (UTS), elongation at break (ϵ_b), and strain energy density at break (U_b), as well as modulus and tear strength, all increase as mean bead diameter decreases. Even with relatively small bead diameter ($25\,\mu$m), UTS and U_b are lower than that of the unfilled compound, although modulus and tear strength are higher [2].

Studies have shown that UTS and U_b can be improved by increasing the degree of bead to matrix bonding [3]. However, little effect on the tear strength was observed. It was suggested that rupture of these materials occurs by the tearing of flaws associated with large dewetted particles [3]. Similar results have been shown in glass bead–polyacrylate systems [4]. In styrene–butadiene (SBR) systems extensive dewetting of the beads causes the stress–strain response of the system to approach that of the gum. Thus no real changes in UTS or ϵ_b were observed [5].

When fine polymeric fillers (particle size 200 to 50 nm) were incorporated into SBR both UTS and tear strength increased. The magnitude of the reinforcement is determined by the filler's ability to dissipate energy. This may be improved by increasing the filler modulus, its adhesion to the matrix and its surface to volume ratio (specific surface area) [6].

The presence of fillers in an elastic matrix causes stress magnification. For hard, well-bonded fillers there is a large stress concentration at the polar interface, although the principal stress maxima occurs some finite distance above the pole. If the particle is unbonded the principal stress maxima occurs at the equatorial interface

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[7]. Similar results have been reported for fillers which are harder and softer than the matrix [8].

1.3. Two-phase elastomers

In a study of two-phase BR–EPDM blends, Hamed [9] found that the interfacial adhesion had a significant effect on the failure properties. If interfacial adhesion is high, a propagating tear will not deviate at the phase boundary. This results in a blend with a U_b equal to the average of the two components. When interfacial adhesion is low, tear deviation will occur. If the size of the dispersed domains is small enough this will result in reinforcement of the continuous phase due to the higher apparent tear strength and increased energy dissipation.

1.4. The use of recycled rubber "crumb" as a filler

Fine rubber crumb (with average particle size of 500 μm or less) has been widely reported as a filler of new rubber compounds. When recycled into its "parent" compound at levels of 10 to 20 wt %, significant losses in UTS and ϵ_b are observed. This decline in ultimate properties increases with increasing filler loading and particle size [10–12]. Little effect on the tear strength has been found [10]. If the crumb is fine enough (i.e. less than 20 μm), up to 30 wt % may be incorporated into critical components such as automobile tyres without significant losses in performance [13].

In previous studies we have compared the performance of crumb prepared by a variety of processes. It was found that the UTS increased as the surface area of the crumb increased. From examination of the fracture surfaces, it was proposed that these materials' poor mechanical performance results from low levels of adhesion between the crumb and new rubber. On straining, dewetting leads to void formation. Growth of these voids results in catastrophic failure at low stresses and strains [14].

The particle size effects found in these materials are similar to those found in elastomers containing hard fillers. In this paper we describe the effect of filler modulus and filler to matrix adhesion.

2. Experimental procedure

2.1. Filler preparation

Four BR ("Austrapol 1220") compounds containing varying amounts of carbon black were prepared in a "Haake Rheomix" and cured at 145° C for 60 min. The resulting pads were then shredded and passed through a "Van Gelder" 25 mm x 125 mm cross-beat mill equipped with a 1 mm screen. The mill was cooled to $-125°$ C with a controlled source of liquid nitrogen. Crumb from the mill had moderate surface structure and was used without further change. Table I gives the filler formulations and mechanical properties after 120 min cure. This allows for the secondary curing which occurs when the crumb is incorporated into the new compound.

2.2. Preparation of filled compounds

Two types of filled compound were prepared and each type contained from 2.5 to 25 vol % filler. For type 1 compounds, the filler, BR and peroxide curative ("Dicup 40 C") were mixed in the internal mixer, operating at 60 rpm and 30° C, for 10 min. In type 2 compounds the filler was mixed with a black-filled masterbatch. The masterbatch had been prepared previously on a two roll mill and contained 50 parts carbon black (International Reference Black no. 5) and 0.43 parts Dicup 40 C per 100 parts polybutadiene. Both types were cured at 145° C for 60 min. The mechanical properties of the unfilled and filled compounds are given in Table II.

TABLE I Filler compounds

	A	B	C	D
BR (Austrapol 1220)	100	100	100	100
Carbon black (IRB#5)	75	50	25	12.5
Dicup 40C	0.54	0.43	0.43	0.43
Hardness (Shore A)	72	46	40	31
E_{100} (MPa)	5.38	1.43	0.96	0.67
σ_b (MPa)	5.14	5.10	4.91	2.87
ϵ_b (%)	96	310	382	459
U_b (MJ m^3)	2.94	6.18	7.74	5.81
Tear strength (kJ m^{-2}) 5 mm min^{-1}	3.87	2.32	2.13	1.76

TABLE II Tensile properties

Masterbatch compound	Filler	Volume fraction, ϕ	Code	UTS (MPa)	ϵ_b	U_b (MJ m^3)
1*	–	–	1	2.44 ± 0.13	2.88 ± 0.37	3.69 ± 1.24
1	A	0.25	1A/25	1.69 ± 0.26	2.04 ± 0.37	2.00 ± 0.30
1	B	0.25	1B/25	2.35 ± 0.20	3.09 ± 0.18	3.40 ± 0.25
1	C	0.25	1C/25	2.61 ± 0.20	3.69 ± 0.31	4.84 ± 0.44
1	D	0.25	1D/25	2.40 ± 0.13	3.85 ± 0.20	3.24 ± 0.63
1	A	0.05	1A/5	1.55 ± 0.16	1.96 ± 0.17	1.71 ± 0.26
1	B	0.05	1B/5	2.72 ± 0.62	3.10 ± 0.72	3.88 ± 1.30
1	C	0.05	1C/5	2.52 ± 0.42	2.97 ± 0.13	3.64 ± 0.53
1	D	0.05	1D/5	2.82 ± 0.68	3.30 ± 0.45	4.51 ± 1.39
2†	–	–	2	5.07 ± 0.61	4.10 ± 0.25	8.77 ± 1.04
2	A	0.25	2A/25	3.00 ± 0.12	2.38 ± 0.05	3.58 ± 0.38
2	B	0.25	2B/25	3.21 ± 0.08	3.29 ± 0.12	4.65 ± 0.25
2	C	0.25	2C/25	3.26 ± 0.19	3.39 ± 0.18	4.78 ± 0.36
2	D	0.25	2D/25	4.71 ± 0.27	4.19 ± 0.10	7.89 ± 0.24
2	A	0.15	2A/15	3.83 ± 0.01	3.00 ± 0.25	5.07 ± 0.56
2	D	0.15	2D/15	5.42 ± 0.47	4.45 ± 0.26	8.14 ± 2.07
2	A	0.05	2A/5	4.04 ± 0.11	3.39 ± 0.12	5.65 ± 0.89
2	B	0.05	2B/5	5.07 ± 0.41	4.52 ± 0.40	8.01 ± 0.98
2	C	0.05	2C/5	5.54 ± 0.22	4.68 ± 0.33	9.68 ± 1.01
2	D	0.05	2D/5	5.42 ± 0.45	4.16 ± 0.26	9.69 ± 1.38
2	A	0.025	2A/2.5	3.71 ± 0.24	3.81 ± 0.05	
2	D	0.025	2D/2.5	5.15 ± 0.55	4.30 ± 0.56	

*Compound hardness = 41 Shore A degrees.
†Compound hardness = 40 Shore A degrees.

All tensile tests were carried in general accordance with ASTM D412 using Type C dumb-bell test pieces and an Instron 1115 Universal Testing machine equipped with a "POGO" long-travel extensometer. Duplicate pads were prepared for compounds containing 25 vol% filler and so data reported are the average of eight individual tests for these compounds. For the remaining compounds, four tests were carried out. Errors bars on graphs represent the standard deviation.

2.3. Preparation of peel specimens

Peel tests were carried out on cloth-backed sandwich specimens as shown in Fig. 1. Cloth-backed strips of the filler compounds were compressed in moulds with the uncured masterbatch compounds and cloth-backing. They were then cured under the same conditions as filled compounds. Peel strengths were determined at grip separation rates of 500, 50, and 5 mm min^{-1}. The adhesive energy, G, was determined using Equation 1 [15]:

$$G = 2F/W \tag{1}$$

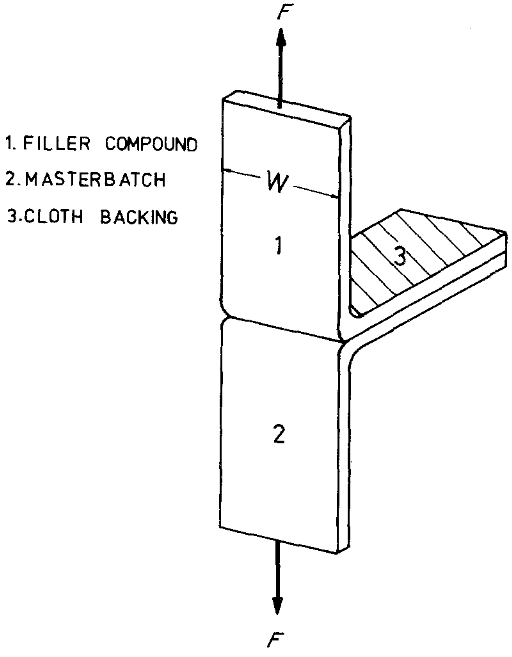

Figure 1 Peel test specimen.

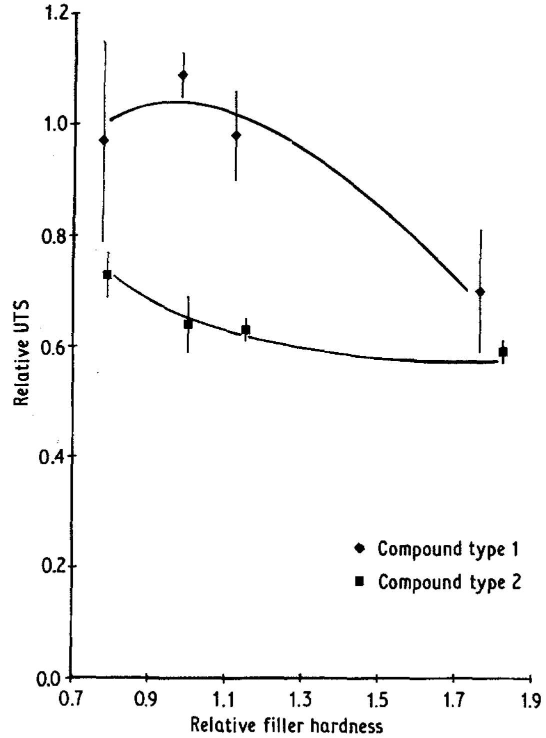

Figure 2 Relative UTS plotted against relative filler hardness.

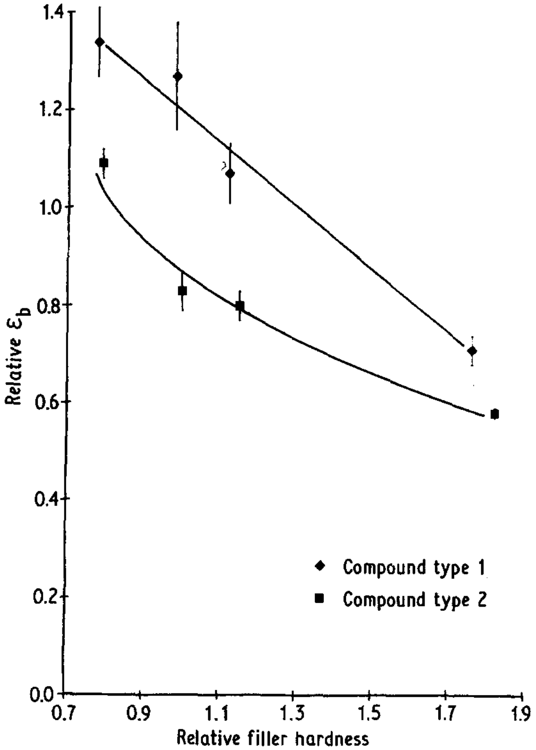

Figure 3 Relative ϵ_b plotted against relative filler hardness.

where F is the peel force and W the specimen width.

2.4. Electron microscopy

Electron micrographs of uncoated samples were taken with an ISI 100A scanning electron microscope equipped with a "Robinson" back-scatter detector. Complementary fracture surfaces were mounted side-by-side to enhance interpretation.

3. Results

3.1. Tensile properties

Incorporation of 5 vol% of the softer fillers (B, C, and D) caused only small changes in the UTS of both type 1 and type 2 compounds. However, the presence of the hardest filler, A, at this or lower loadings (2.5 vol%) leads to a significant reduction in the UTS of both compounds. This result is in accord with the work of others [10–12] in which small amounts of crumb with similar properties to the matrix caused only slight reductions in the compound's UTS.

The relative UTS (compound UTS/masterbatch UTS) of compounds containing 25 vol% filler are given in Fig. 2 as a function of relative filler hardness. Even at this loading, fillers B, C, and D have little effect on the UTS of type 1 compounds, with again only the hardest filler, A, causing a significant reduction. All type 2 compounds, however, suffer a reduction in UTS (their relative UTS is less than 1). For these compounds UTS decreases as filler hardness increases.

At filler loadings of 5 vol%, ϵ_b behaves in the same manner as UTS, with only filler A causing any significant loss. At 25 vol% loading, ϵ_b decreases as filler hardness increases (Fig. 3). Type 1 compounds, except that containing filler A, have ϵ_b greater than that of the unfilled masterbatch (relative ϵ_b greater than 1). Type 2 compounds, although showing the same trend as type 1, have much lower relative ϵ_b values.

The stress–strain relationships (Fig. 4) indicate that as filler hardness increases the compound modulus also increases, whilst the ϵ_b falls. Decreasing the loading of filler A leads to a fall in modulus and an increase in ϵ_b (Fig. 5). Changing the loading of the softest filler, D, however, has little effect on either modulus or ϵ_b.

3.2. Peel test

All peel tests on type 1 filler specimens resulted in the cohesive failure of the type 1 masterbatch, indicating a high relative interfacial adhesion. The

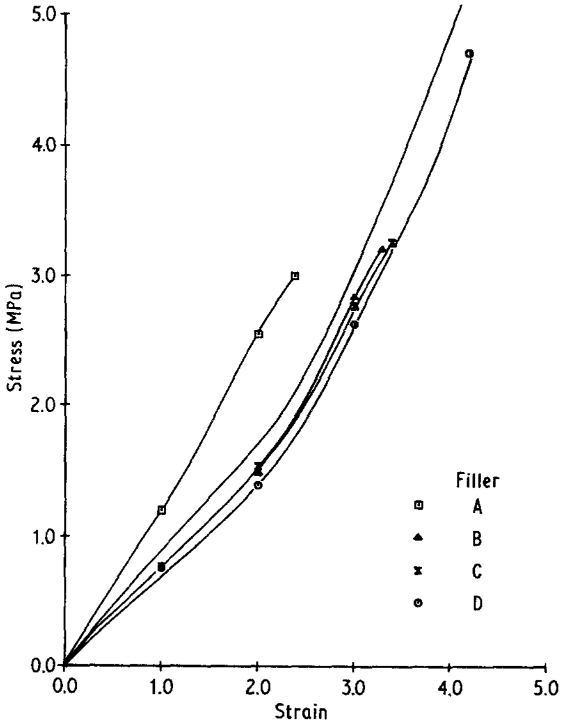

Figure 4 Stress–strain response of type 2 compounds containing 25 vol % filler.

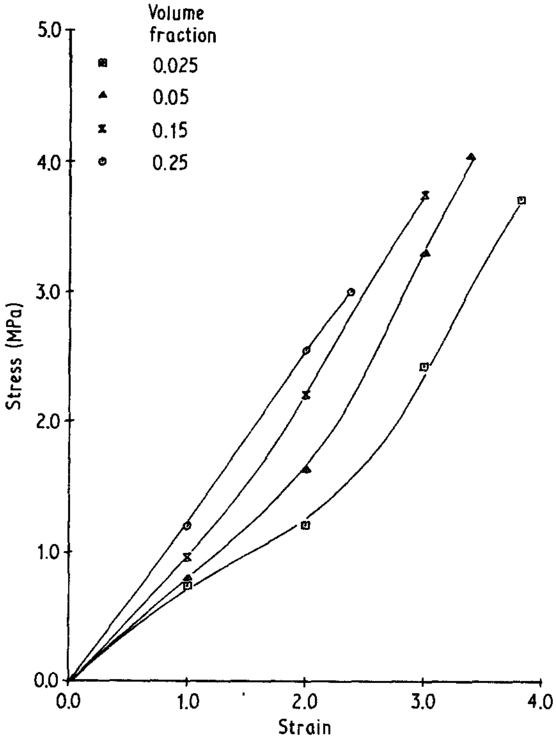

Figure 5 Stress–strain response of type 2 compounds containing 2.5 to 25 vol % filler A.

results of tests on the type 2 filler specimens are given in Table III. The adhesive strength varied from 0.14 to 0.36 times the tear strength of the type 2 masterbatch indicating a low relative adhesion.

3.3. Fracture morphology

The fracture surfaces of both types of compounds became smoother with decreasing filler hardness as is shown in Fig. 6. As filler loading decreases the surfaces become flatter overall, but individual features become more apparent. Fig. 7 shows the fracture initiation site of compound 2A/2.5. Similar features were also found when the type 2 compounds contained filler B. The initiation sites in compounds containing fillers C and D were found to be much flatter, as shown in Fig. 8. Some evidence of dewetting is also found in these micrographs and is marked DW.

TABLE III Peel strength adhesive energy, G (kJ m^{-2})

Filler	Grip separation rate (mm min^{-1})		
	5	50	500
A	1500	2540	3900
B	1230	2340	3060
C	570	1030	1630
D	570	810	1390

The fracture initiation sites in type 1 compounds were not easily discerned, although evidence of filler rupture (marked "R" in Fig. 9) was seen. This was not apparent in type 2 compounds.

4. Discussion

4.1. Effect of filler–matrix adhesion

The difference in the mechanical behaviour of the two types of compound may be attributed to variation in filler–matrix adhesion. Type 1 compounds, which have the highest interfacial adhesion as measured by peel tests, also have the highest relative UTS and ϵ_b. According to Hamed [9] the U_b of type 1 compounds should approach a value predicted by Equation 2:

$$U_b = U_{bf}\phi_f + U_{bm}\phi_m \tag{2}$$

where U_{bf} and ϕ_f are the U_b and volume fraction of the filler and U_{bm} and ϕ_m are those of the matrix. A plot of compound U_b against filler U_b for type 1 compounds gives a linear relationship (correlation coefficient = 0.97) as shown in Fig. 10: the slope of the line, 0.63, is somewhat greater

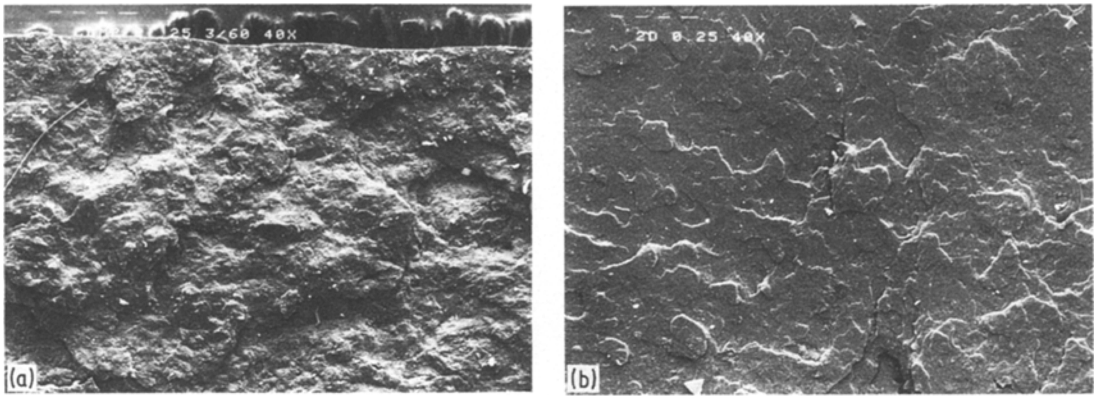

Figure 6 (a) Fracture surface of compound 2A/25. Original magnification × 40. (b) Fracture surface of compound 2D/25. Original magnification × 40.

than the value of 0.25 predicted in Equation 2. After allowing for experimental error, compounds 1A and 1B show the greatest deviation from predicted behaviour. These compounds have rough fracture surfaces indicating that tear deviation is occurring. Given the comparatively high tear strength of the filler and the rough fracture morphology of these two compounds it would appear that catastrophic failure takes place mainly in the matrix. This results in a U_b lower than that predicted in Equation 2.

The predominant factors influencing the behaviour of type 2 compounds are the relative filler hardness and the low interfacial adhesion. For hard fillers, the stress experienced by the polar interface, where dewetting is expected, will be greater than the applied stress [7]. This leads to interfacial failure at lower applied strains, the voids thus formed leading to catastrophic failure at values of U_b lower than those predicted by Equation 2. This behaviour is observed in type 2 compounds containing the hard fillers A, B, and C (see Table IV). When the filler is softer than the matrix the stress at the polar interface will be less than the applied stress [8] and the amount of dewetting will be reduced. In type 2 compounds containing the softest filler D, dewetting is negligible as is tear deviation. This results in a flat fracture topography and a U_b value approaching that predicted by Equation 2 (see Table IV).

4.2. Compound modulus

While the ultimate properties are of prime importance, the modulus of an elastomer may also determine its suitability for a particular application. The relative modulus (compound modulus/masterbatch modulus) at 100% elongation of type 1 compounds is shown in Fig. 11 as a function of filler modulus.

Dickie [16] has reviewed methods of predicting

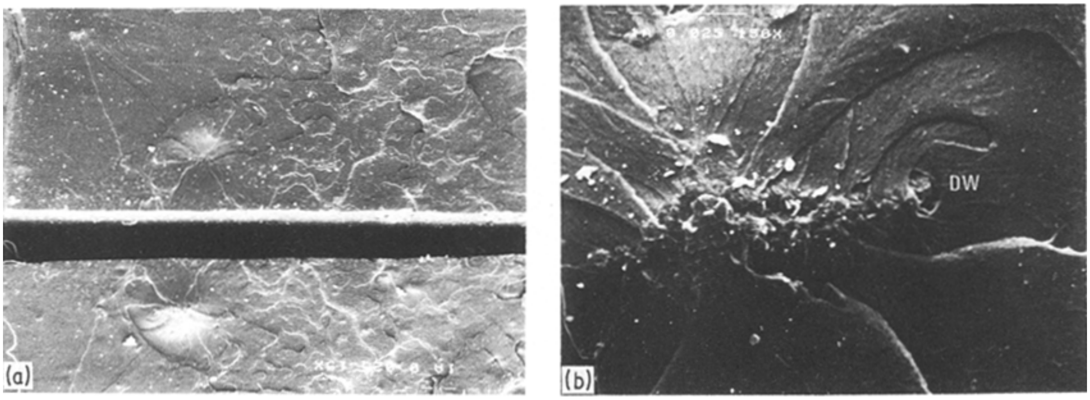

Figure 7 Fracture initiation site compound 2A/2.5. Original magnification (a) × 40, (b) × 150.

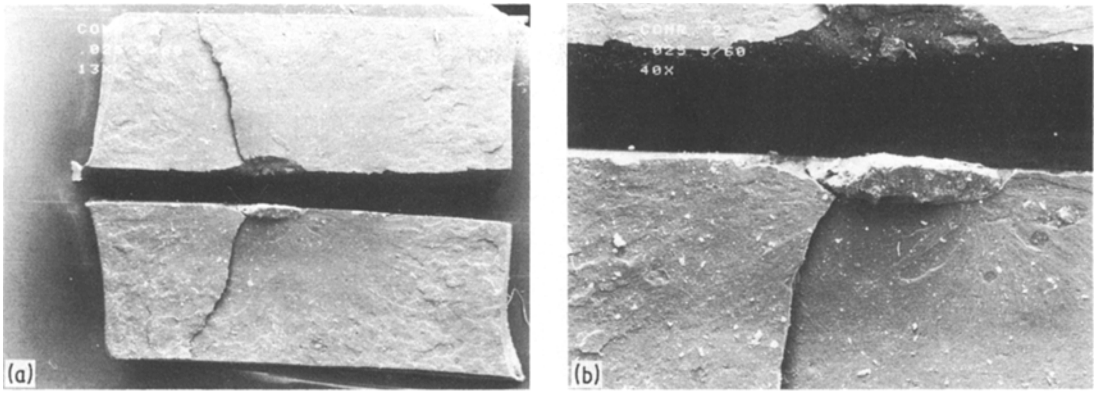

Figure 8 Fracture initiation site compound 2D/2.5. Original magnification (a) × 13, (b) × 40.

the modulus of composite materials. One of the simplest techniques is to predict the upper and lower limits using parallel and series models defined by Equation 3 and 4, respectively:

$$E_{\text{upper}} = E_f \phi_f + E_m \phi_m \quad (3)$$

$$E_{\text{lower}} = 1/(\phi_f/E_f + \phi_m/E_m) \quad (4)$$

where E_f and ϕ_f are the modulus and volume fraction of the filler and E_m and ϕ_m are those of the matrix. The solid lines in Fig. 11 are defined by Equations 3 and 4.

When filler modulus is similar to that of the matrix, no distinction can be made between the two models. However, for the harder fillers A and B the values lie close to the series prediction. This is the limit approached when only the softer phase is continuous [17], as is also the case in these compounds. Type 2 compounds generally have moduli lower than the series model, perhaps reflecting lower interfacial adhesion.

4.3. Fracture morphology

The observed differences in fracture morphology of the compounds may be explained in terms of the relative tear strengths of fillers compared to the matrix, although the degree of adhesion is also expected to have some effect. When the tear strength of the filler is low compared to the matrix, a propagating tear will not deviate at the filler–matrix boundary. This results in a flat fracture topography and a U_b approaching the value predicted by Equation 2. This is the observed behaviour of compounds 1C, 1D, and 2D. When the filler tear strength is high, tear deviation and dewetting will occur giving a rough fracture topography and lower values of U_b.

TABLE IV Strain energy densities (MJ m^{-3})

Compound	Value predicted by Equation 2	Actual value
2A/25	7.31	3.58 ± 0.38
2B/25	8.12	4.65 ± 0.25
2C/25	8.51	4.78 ± 0.36
2D/25	8.03	7.89 ± 0.24

The fracture initiation sites in compounds containing fillers A and B have a mound-depression morphology as shown in Fig. 7. It appears that catastrophic tearing has initiated at the pole of a filler particle where dewetting is expected. The tear then follows the path of the stress maxima through the matrix. This is consistent with the published stress birefringence studies of Oberth [7] which show that the stress distribution changes when dewetting occurs. The resulting distribution would give a similar fracture topography. Higher magnification micrographs show that the matrix compound has pulled away from the filler particle (marked "DW" in Fig. 7).

The tear initiation sites in compounds containing filler D are usually associated with edge flaws. In Fig. 8 this appears to be a filler particle. Catastrophic failure was initiated at the equatorial regions of the particle, but it is not clear whether this occurred before or after dewetting.

As mentioned earlier, the fracture initiation sites in type 1 compounds are not easily determined from the fracture topographs. High magnification studies show little signs of dewetting. The high interfacial adhesion resulted in filler failure not previously found in type 2 compounds, this being unexpected given the relative high tear

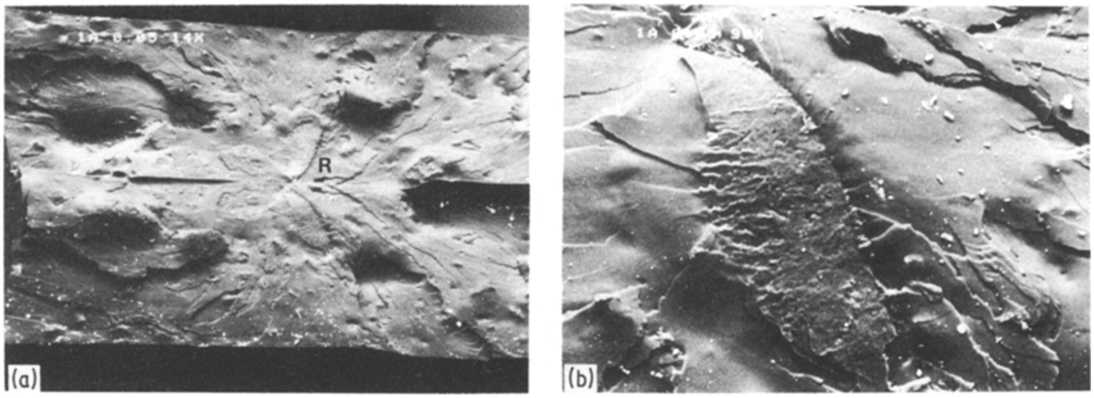

Figure 9 Fracture surface compound 1A/5. Original magnification (a) X 14, (b) X 90.

strength of the harder fillers compared to the type 1 masterbatch. Considering the low ϵ_b of filler A (1.98) it appears that filler rupture may initiate final failure of compound 1A/5, as seen in the fracture topography in Fig. 9.

5. Conclusions

We conclude from these studies that when interfacial adhesion is high the U_b of the filled compounds is linearly related to the U_b of the filler, although incorporation of excessively hard fillers will result in some deviation from the predicted behaviour. If the interfacial adhesion is low the compound U_b is much lower than predicted, and is not a linear function of filler U_b. It is suggested that failure of these materials occurs by the growth of voids produced by filler dewetting. The degree of dewetting increases as filler hardness increases.

Increasing the filler-to-matrix bonding offers an alternative method (to expensive particle-size

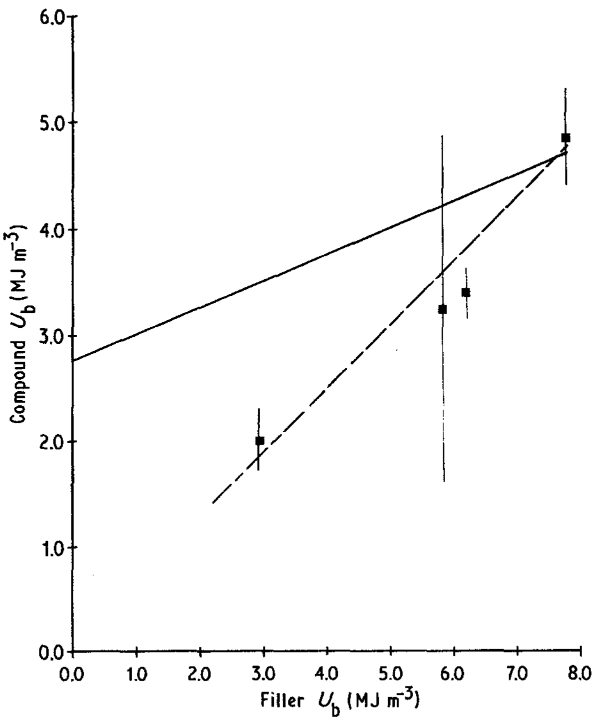

Figure 10 Compound U_b plotted against filler U_b, for type 1 compounds containing 25 vol% filler. Solid line represents Equation 2.

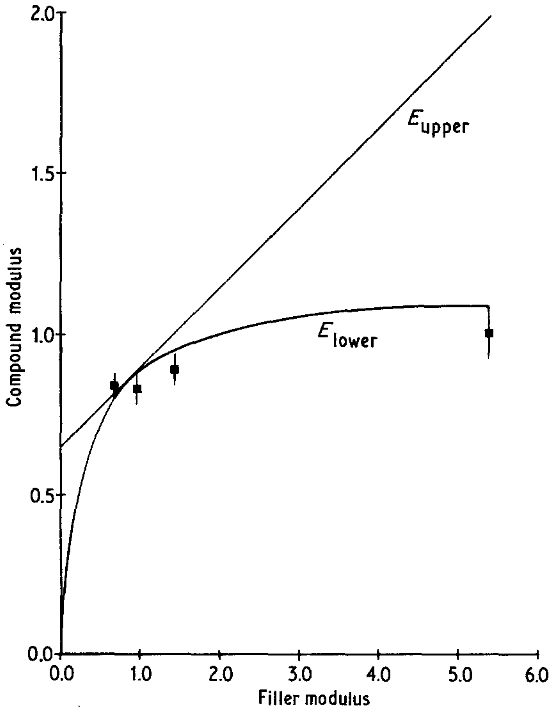

Figure 11 Compound modulus plotted against filler modulus for type 1 compounds containing 25 vol% filler. Solid lines represent the upper and lower limits as determined using Equations 3 and 4.

reduction) for improving the mechanical properties of rubber compounds containing rubber crumb fillers. The authors are currently investigating simple chemical treatments which when applied to the crumb will improve physical or chemical bonding between filler and matrix.

In a subsequent paper [18] we present tear strength results, together with macroscopic evidence supporting the above failure mechanism.

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